Corrosion of Reactor Components

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ATR National Scientific User Facility
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Cost of Corrosion in NPPs

Table 15. Summary of total cost of corrosion to the electrical utilities industry.

FACILITY	REASON FOR CORROSION COST	CORROSION COST PER YEAR ($ x billion)
Nuclear	O&M	2.013
	Depreciation	1.546
	Forced Outage	0.670
	SUBTOTAL	**$4.229**
Fossil Fuel	O&M	0.698
	Depreciation	1.214
	Forced Outage	0
	SUBTOTAL	**$1.912**
Hydraulic & Other Products	O&M	0.075
	Depreciation	0.066
	Forced Outage	0
	SUBTOTAL	**$0.141**
Transmission & Distribution	O&M	0
	Depreciation	0.607
	Forced Outage	0
	SUBTOTAL	**$0.607**
	TOTAL	**$6.889 billion**

$17.27 billion
EPRI estimate

G. Koch, CC Technologies

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Outline

- Forms of corrosion
- Corrosion basics
- Materials in reactor components
- Environments for reactor components
- Operational experience with corrosion of reactor components
- Summary

Forms of Corrosion

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Types of Corrosion Damage

- **General Corrosion**
- **Galvanic Corrosion**
  - Dissimilar “Metals” and an Electrolyte
- **Environmentally Induced Cracking (SCC, Corrosion Fatigue)**
  - Combination of Tensile Stress, Specific Environment, Material
- **Hydrogen Damage**
- **Dealloying**
- **Localized Corrosion**
  - Pitting
  - Crevice Corrosion
  - Intergranular Corrosion
- **Flow Assisted Corrosion**
  - Combination of Flow Velocity and Corrosion
- **Erosion-Corrosion**
  - Combination of Erosive Environment, Flow and Corrosion
- **Microbial Induced Corrosion**

Corrosion in LWRs

- General Corrosion, cation release & fouling
- Flow Assisted (Accelerated) Corrosion
- Erosion-corrosion (Steam cutting)
- Localized corrosion (Pitting, crevice and microbial corrosion)
- Stress corrosion cracking and hydrogen embrittlement
- Corrosion fatigue

Corrosion Basics

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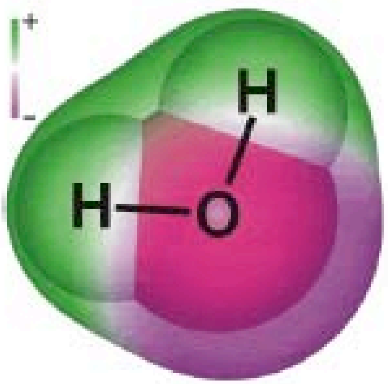
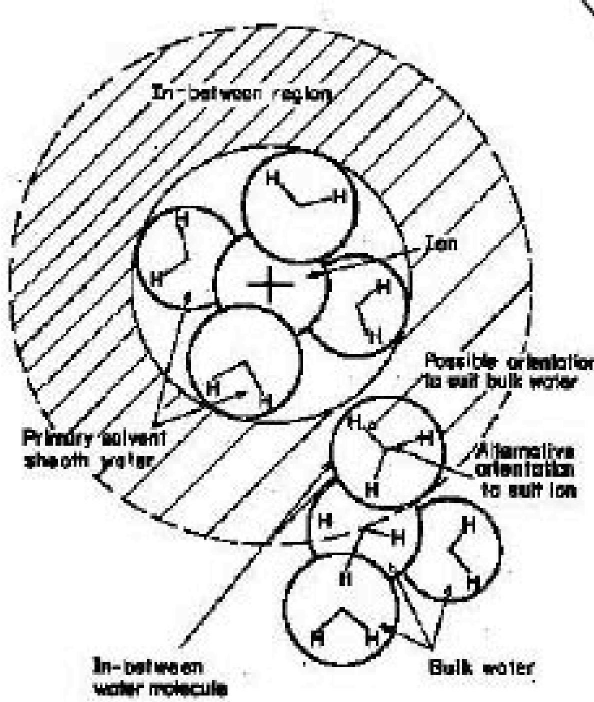
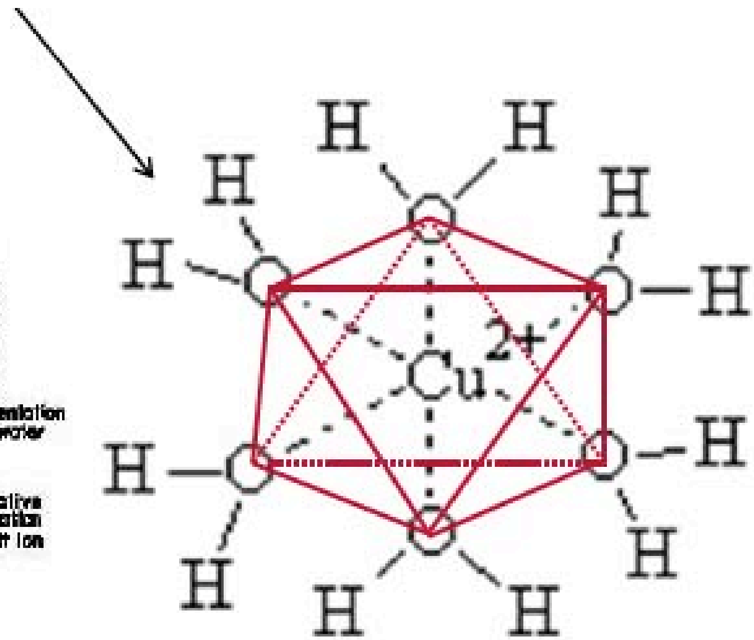
Electrochemical Nature of Corrosion

- In water, most solutes are dissociated into anions and cations
- Due to the dipolar character of the water molecule, positive cations are bound to a sheath of water molecules called the solvation layer
  - Formation of a complex solvated cation $Mz^{+}(H_2O)_n$ with n=6 in many cases
  - Metallic cations are at the center of octahedra that are the base element of hydroxides or oxides formed by hydrolysis



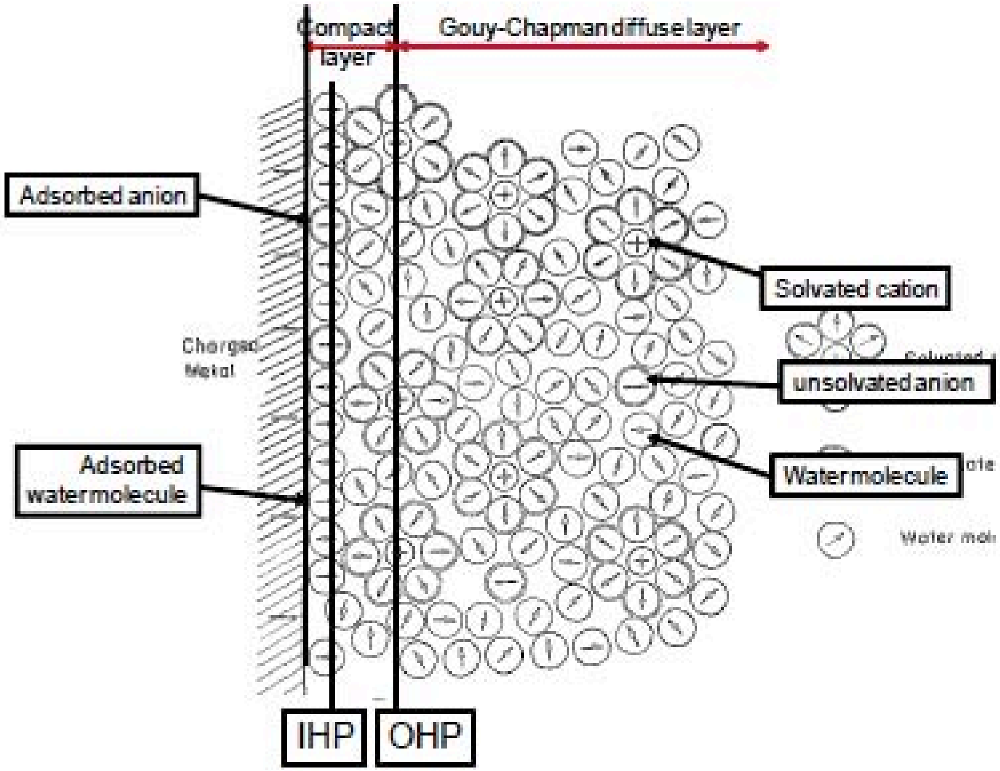
The approximate shape and charge distribution of water

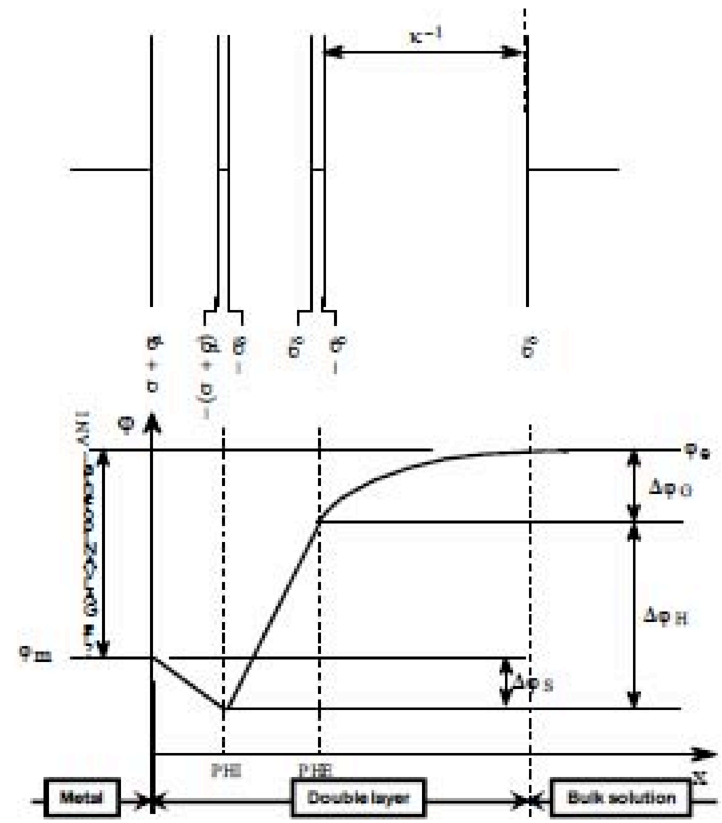




Courtesy Pierre Combrade

Electrochemical Nature of Corrosion





- When a metal is immersed in an aqueous solution,
  - electrical charges accumulate at the interface, both in the metal and in the solution, creating a so-called "electrical double layer" that can be represented as a series of capacitors.
  - A potential difference appears between the metal and the aqueous solution
    - Metal/solution potential (electrode potential)

$$E = \Phi_m = \Phi_s$$

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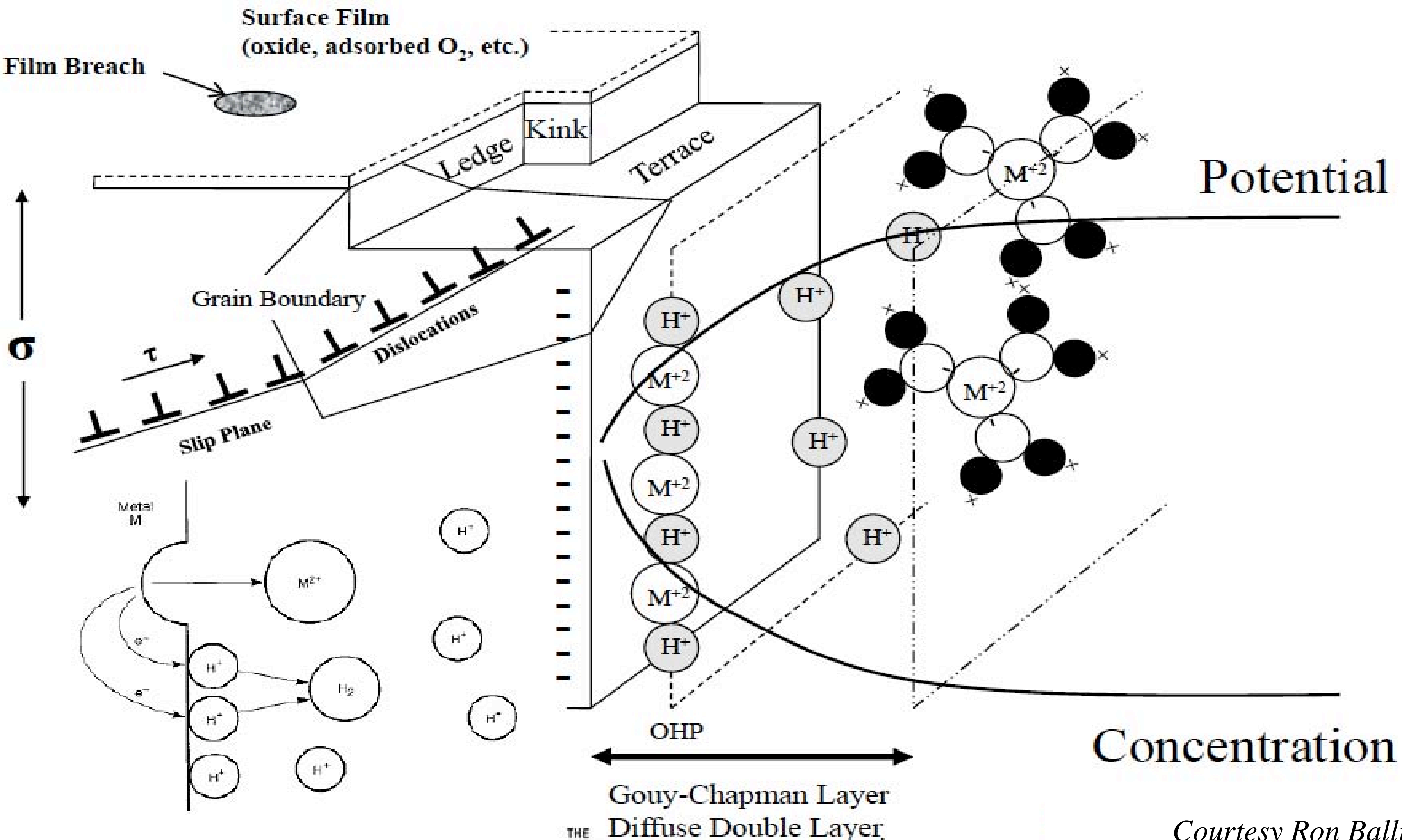
A Closer Look at the Metal-Solution Interface



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The Metal

- Uniform corrosion isn't really "uniform":Terrace-Ledge-Kink (TLK).
- Active sites present (preferred anodes)-grain boundaries, dislocations, precipitates/other phases, etc.
- Film formation
- Film instability
- Occluded regions (crevices, pits, etc.)
- Crystallographic effects
- Plastic deformation-dislocations exiting surface

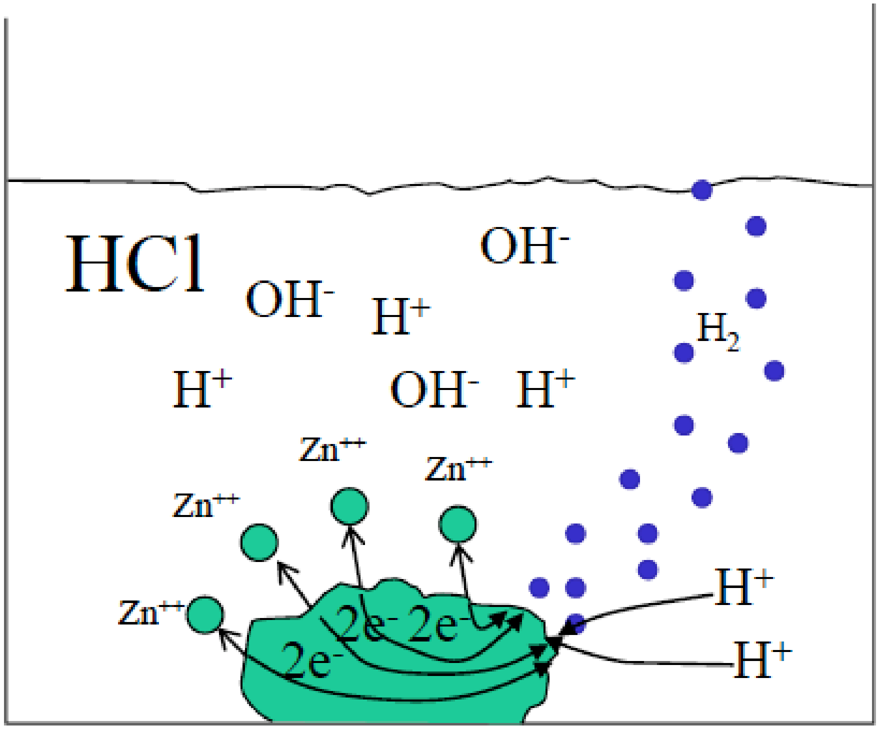
The Water

- Dissolved metal ions
- Other species in solution, O_2, H^+, OH^-
- Water
  - Water will play a role, polar molecule
  - Hydration sheath
- Concentration gradients (Concentration polarization)
- Potential gradients

Metal/Water Interface

- Multiple Reactions
  - Oxidation-Metal Dissolution
- Dissolution process has an “activation” barrier.
  - Reduction (hydrogen, oxygen)
- Hydrogen (or oxygen) reduction not so simple-multi step process
- Double Layer formation
  - Net negative charge on metal balances by net positive charge from the aqueous solution
- Film formation-”passivation”
  - Chemisorbed
  - Adsorbed

Electrochemical Corrosion



Drop a piece of Zn Metal into 1M HCl

Zinc goes into solution (Oxidation-Anode)

$$Zn \Rightarrow Zn^{++} + 2e^{-}$$

Hydrogen gas is released (Reduction-Cathode)

$$2H^{+} + 2e^{-} \Rightarrow H_2(gas)$$

Note: Electrons are released by oxidation of Zn and consumed by hydrogen Reduction-Charge cannot be stored.

$$\sum_A = \sum_C$$

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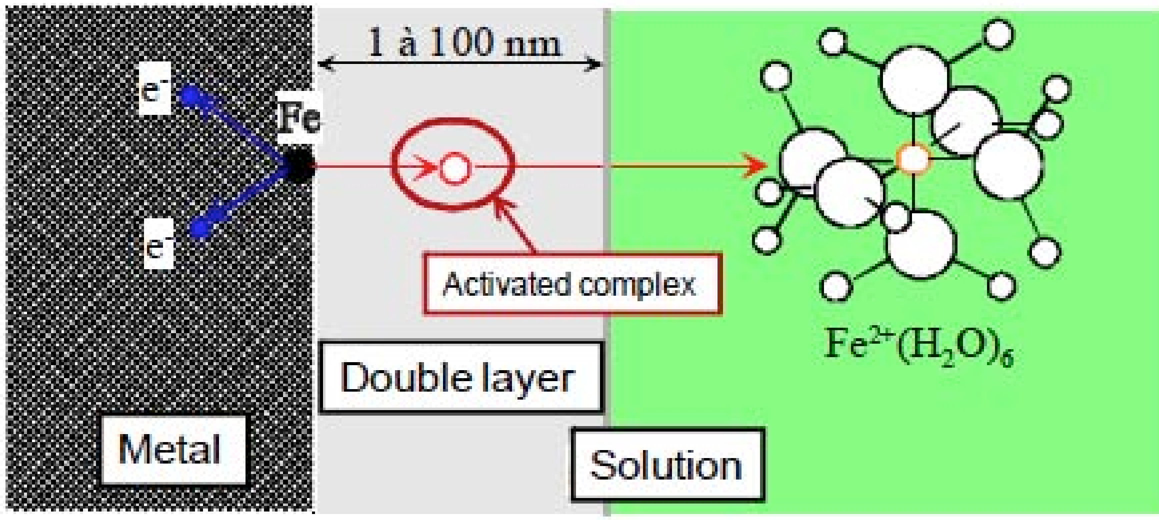
Electrochemical Reactions

Reactions occur that involve charge transfer between the metal and solution.



- Anodic (Oxidation)
  - General: $M \rightarrow M^{n+} + ne^-$
  - $Fe \rightarrow Fe^{2+} + 2e^-$
  - $Fe^{2+} \rightarrow Fe^{3+} + e^-$
  - $Ni \rightarrow Ni^{2+} + 2e^-$
  - $Al \rightarrow Al^{3+} + 3e^-$
- Cathodic (Reduction) Reactions
  - $2H^+ + 2e^- \rightarrow H_2(g)$, Hydrogen Reduction
  - $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, Oxygen Reduction-Neutral of Basic Solutions
  - $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, Oxygen Reduction-Acid Solutions
  - $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
  - $M^{n+} + ne^- \rightarrow M$, Metal Deposition

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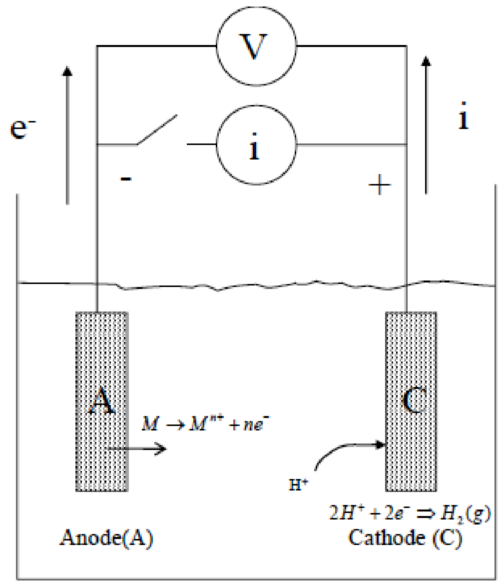
Electrochemical Reactions Produce an Electrical Current

- Charge transfer gives rise to:
  - an electrical current in the metal
  - an ionic current in the solution



- Electron flow in external circuit from anode to cathode
- BUT: Current in a circuit by definition flows from positive to negative
- Anode is thus negative
- Cathode is thus positive

- Faraday's law gives the reaction rate in terms for a current intensity through the metal/solution interface

$$w = kIt$$

w=weight of metal reacted (g)
k=constant (g/coul)
I=current (coul/sec)
t=time (sec)

- Electrical neutrality of each phase requires that no net charge accumulates, therefore:

$$\Sigma i_{\text{Anodic}} = \Sigma i_{\text{cathodic}} \quad \text{or} \quad \Sigma i_{\text{Oxidation}} = \Sigma i_{\text{Reduction}}$$

THERMODYNAMICS

How do we know whether a reaction will occur?

$$(1)\quad Cu + H_2O(l) + \frac{1}{2}O_2(g) \Rightarrow Cu(OH)_2(s) \qquad \Delta G^0 = -1.19x10^5\, J/Mole$$

$$(2)\quad Mg + H_2O(l) + \frac{1}{2}O_2(g) \Rightarrow Mg(OH)_2(s) \qquad \Delta G^0 = -5.96x10^5\, J/Mole$$

$$(3)\quad Au + \frac{3}{2}H_2O(l) + \frac{3}{4}O_2(g) \Rightarrow Au(OH)_3(s) \qquad \Delta G^0 = 6.5x10^4\, J/Mole$$

Reactions (1) and (2) have a negative ΔG and therefore will occur spontaneously. Reaction (3) has a positive ΔG and is therefore will not occur.

Relationship between Free Energy and Potential

Relationship Between ΔG and Potential (E)

$$\Delta G = -nFE$$

- F = Faraday's Constant (96,500 Coulomb/Equivalent)
- n = Number of electrons involved in the reaction

Consider the general reaction:

$$lL + mM + \ldots.. \Rightarrow qQ + rR + \ldots\ldots$$

l, m, q, r = # moles of a substance

The change in free energy, ΔG, for the reaction is:

$$\Delta G = \left(qG_Q + rG_R + \ldots\right) \quad \left(lG_L + mG_m + \ldots\right)$$

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Nernst Equation

The Nernst equation gives the EMF of a cell.

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_Q^q a_R^r \ldots}{a_L^l a_M^m \ldots}$$

E^0 is the Standard potential defined at room temperature and atmospheric pressure.

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Reduction potentials

Oxidation potentials

Anodic - exhibits greater tendency to lose electrons			
Reduction Reaction	E^o (V)	Oxidation Reaction	E^o (V)
$Li^+ + e^- \rightarrow Li$	-3.04	$Li \rightarrow Li^+ + e^-$	3.04
$K^+ + e^- \rightarrow K$	-2.92	$K \rightarrow K^+ + e^-$	2.92
$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90	$Ba \rightarrow Ba^{2+} + 2e^-$	2.90
$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87	$Ca \rightarrow Ca^{2+} + 2e^-$	2.87
$Na^+ + e^- \rightarrow Na$	-2.71	$Na \rightarrow Na^+ + e^-$	2.71
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37	$Mg \rightarrow Mg^{2+} + 2e^-$	2.37
$Al^{3+} + 3e^- \rightarrow Al$	-1.66	$Al \rightarrow Al^{3+} + 3e^-$	1.66
$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18	$Mn \rightarrow Mn^{2+} + 2e^-$	1.18
$2H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$	-0.83	$H_2 + 2\,OH^- \rightarrow 2H_2O + 2e^-$	0.83
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76	$Zn \rightarrow Zn^{2+} + 2e^-$	0.76
$Cr^{2+} + 2e^- \rightarrow Cr$	-0.74	$Cr \rightarrow Cr^{2+} + 2e^-$	0.74
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44	$Fe \rightarrow Fe^{2+} + 2e^-$	0.44
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.41	$Cr \rightarrow Cr^{3+} + 3e^-$	0.41
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40	$Cd \rightarrow Cd^{2+} + 2e^-$	0.40
$Co^{2+} + 2e^- \rightarrow Co$	-0.28	$Co \rightarrow Co^{2+} + 2e^-$	0.28
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25	$Ni \rightarrow Ni^{2+} + 2e^-$	0.25
$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14	$Sn \rightarrow Sn^{2+} + 2e^-$	0.14
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13	$Pb \rightarrow Pb^{2+} + 2e^-$	0.13
$Fe^{3+} + 3e^- \rightarrow Fe$	-0.04	$Fe \rightarrow Fe^{3+} + 3e^-$	0.04
Arbitrary Neutral : H_2			
Reduction Reaction	E^o (V)	Oxidation Reaction	E^o (V)
$2H^+ + 2e^- \rightarrow H_2$	0.00	$H_2 \rightarrow 2H^+ + 2e^-$	0.00

Arbitrary Neutral : H_2			
Reduction Reaction	E^o (V)	Oxidation Reaction	E^o (V)
$2H^+ + 2e^- \rightarrow H_2$	0.00	$H_2 \rightarrow 2H^+ + 2e^-$	0.00
Cathodic - exhibits greater tendency to gain electrons			
Reduction Reaction	E^o (V)	Oxidation Reaction	E^o (V)
$S + 2H^+ + 2e^- \rightarrow H_2S$	0.14	$H_2S \rightarrow S + 2H^+ + 2e^-$	-0.14
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15	$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$	-0.15
$Cu^{2+} + e^- \rightarrow Cu^+$	0.16	$Cu^+ \rightarrow Cu^{2+} + e^-$	-0.16
$SO_4^{2+} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$	0.17	$SO_2 + 2H_2O \rightarrow SO_4^{2+} + 4H^+ + 2e^-$	-0.17
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22	$Ag + Cl^- \rightarrow AgCl + e^-$	-0.22
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34	$Cu \rightarrow Cu^{2+} + 2e^-$	-0.34
$ClO_3^- + H_2O + 2e^- \rightarrow ClO_2^- + 2OH^-$	0.35	$ClO_2^- + 2OH^- \rightarrow ClO_3^- + H_2O + 2e^-$	-0.35
$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$	0.40	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	-0.40
$Cu^+ + e^- \rightarrow Cu$	0.52	$Cu \rightarrow Cu^+ + e^-$	-0.52
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$2I^- \rightarrow I_2 + 2e^-$	-0.54
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	-0.68
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	-0.77
$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	0.78	$NO_2 + H_2O \rightarrow NO_3^- + 2H^+ + e^-$	-0.78
$Hg^{2+} + 2e^- \rightarrow Hg$	0.78	$Hg \rightarrow Hg^{2+} + 2e^-$	-0.78
$Ag^+ + e^- \rightarrow Ag$	0.80	$Ag \rightarrow Ag^+ + e^-$	-0.80
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$NO + 2H_2O \rightarrow NO_3^- + 4H^+ + 3e^-$	-0.96
$Br_2 + 2e^- \rightarrow 2Br^-$	1.06	$2Br^- \rightarrow Br_2 + 2e^-$	-1.06
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	-1.23
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.28	$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$	-1.28
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$	-1.33

Pourbaix (Stability) Diagrams

- Electrode Potential/Ph Diagram-A graphical presentation of the thermodynamic equilibrium states of a metal-electrolyte system
- Lines dividing zones are calculated using Nernst

$$E = E^0 - \frac{RT}{nF}\ln\frac{a_Q^q a_R^r \cdots}{a_L^l a_M^m \cdots} \qquad E = E^0 - 2.303\frac{RT}{nF} Log\frac{[\text{Products}]}{[\text{Reactants}]}$$

- Dividing lines for dissolved species defined for an activity of 10^{-6}
- Horizontal Lines: REDOX (Reduction/Oxidation) reactions. Charge teansfer, ***no pH dependence***. (Includes OH^-, H^+)
- Vertical Lines: No REDOX, No charge transfer, ***pH Dependence.***
- Diagonal Lines: BOTH REDOX, and pH dependence
- NOTE: H_2O, H^+, OH^- always present

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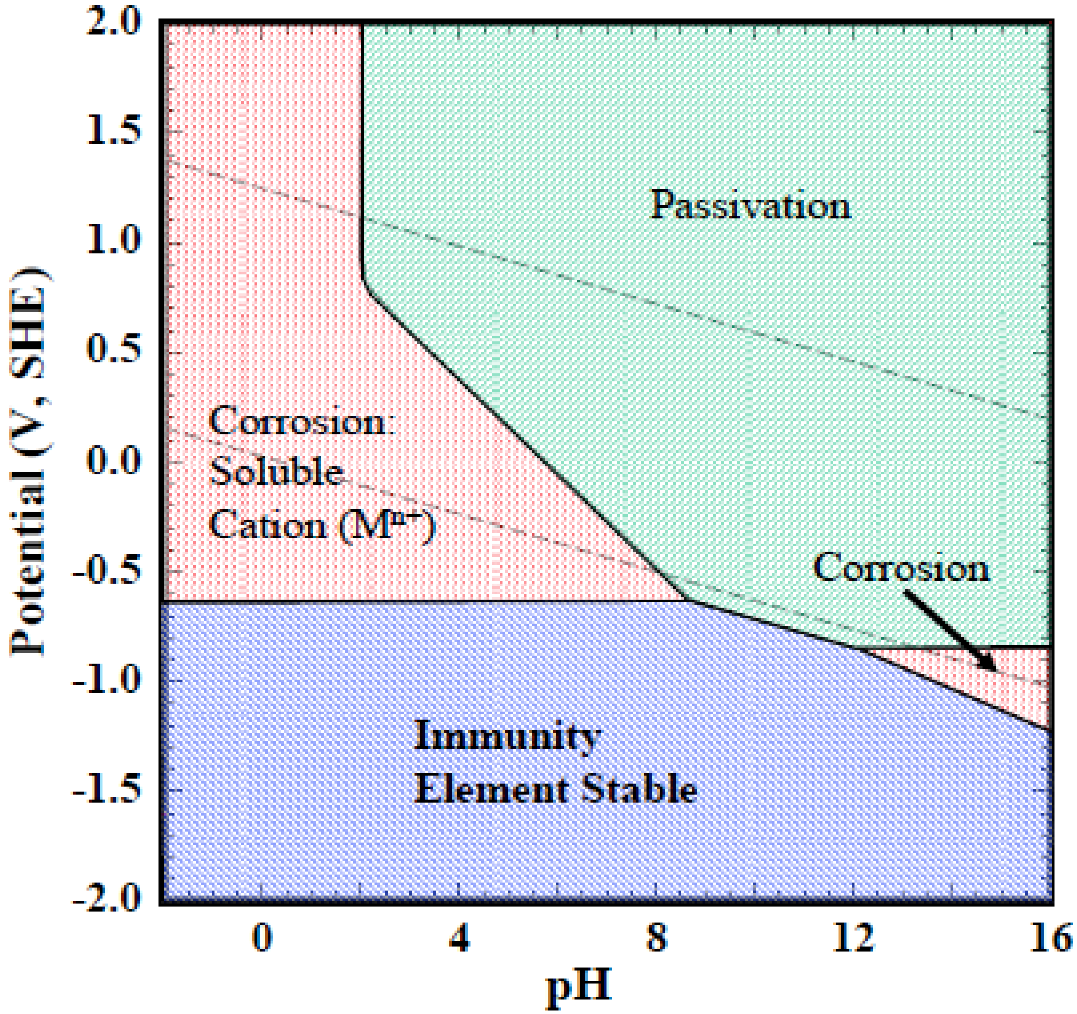
Limitations

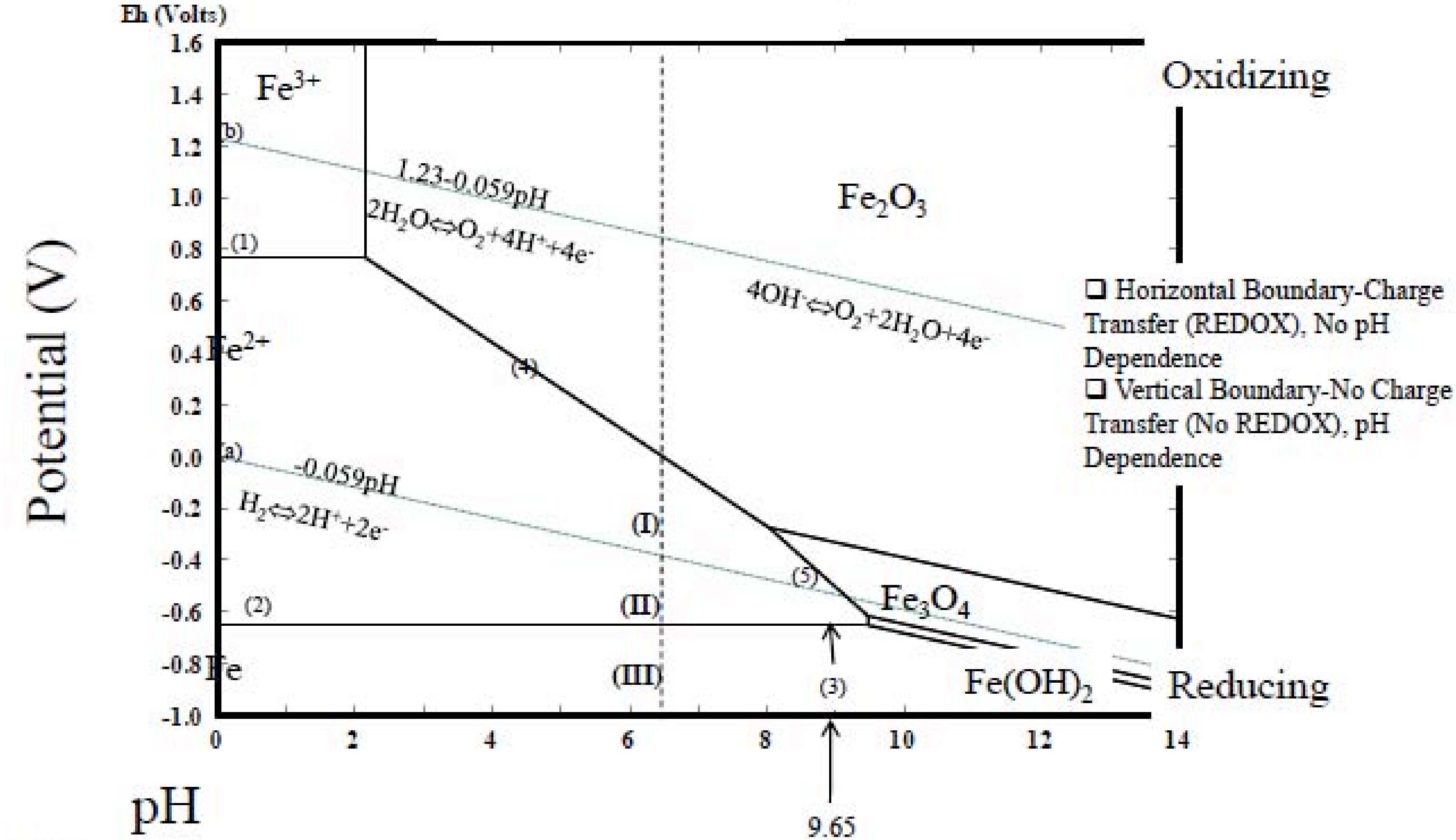
- Diagrams represent EQUILIBRIUM bahavior.
- Diagrams provide no information regarding kinetics
- Most diagrams are for pure metals @ standard conditions in aqueous solutions.
  - High temperature diagrams are available (and can be calculated) as are those for alloys.
- Do not (necessarily) take into account non-ideal behavior

Example of a Pourbaix Diagram



Courtesy Ron Ballinger

Fe-H_2O system at 25°C



- 25°C
- 1 atm
- Boundaries Drawn @ 10^{-6} M

Courtesy Ron Ballinger

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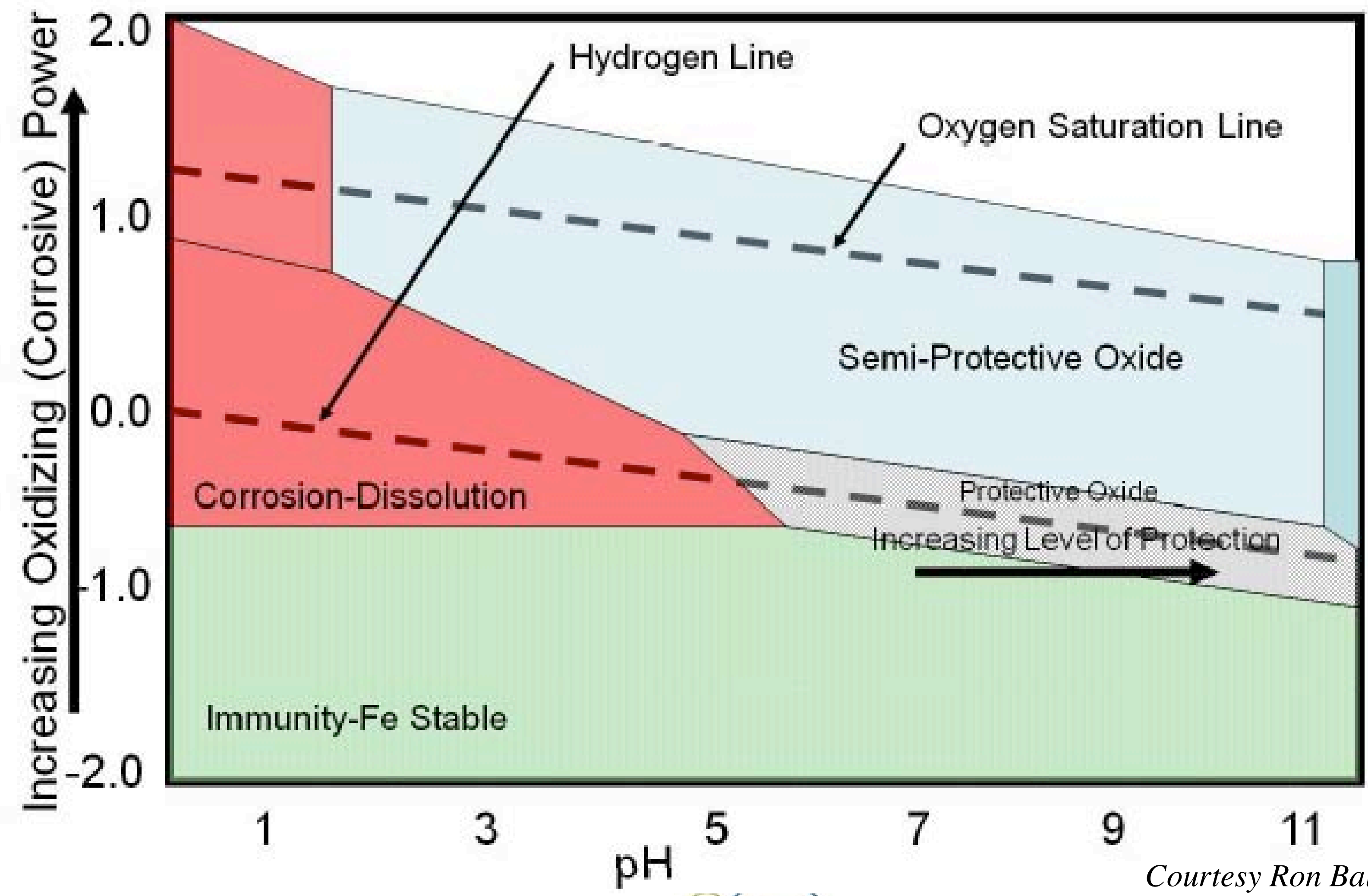
Reactions represented in a Pourbaix diagram

- Reduction of aqueous cations (horizontal line)
  - $M^{n+} + ne^- = M$
- Reduction of metal hydroxide or oxide (sloped line)
  - $M(OH)_n + nH^+ + ne^- = M + nH_2O$
- Reduction of a soluble aqueous anion (sloped line)
  - $MO_m^{n-2m} + 2mH^+ + ne^- = M + mH_2O$
- Change in chemistry with no change in oxidation state (vertical line)
  - $2M^{3+} + 3H_2O = M_2O_3 + 3H_2$

Fe-Water System



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What can Pourbaix diagrams reveal and not reveal about corrosion?

Pourbaix diagrams indicate:

- Regions where corrosion is likely
- Regions where protection may be possible
- Regions where no significant corrosion is possible - immunity

However, Pourbaix diagrams ***do not*** reliably indicate regions of protection by surface oxides

- The existence of a stable oxide does not mean that it will form or that it will be protective
- The nature of the protective passive film is often different from that of bulk oxide phases

Pourbaix diagrams are equilibrium diagrams - they DO NOT give indications of corrosion rates

KINETICS

When the potential of a metal/solution interface differs from the equilibrium potential, a current will flow. The departure from equilibrium potential is called the overpotential, η.

$$\eta = E - E^0$$

The relationship between potential and current is given by the Tafel equations.

$$\eta_c = \beta_c \log \frac{i}{i_0}$$

$$\eta_A = \beta_A \log \frac{i}{i_0}$$

i_0 is the exchange current density and b are Tafel "slopes"

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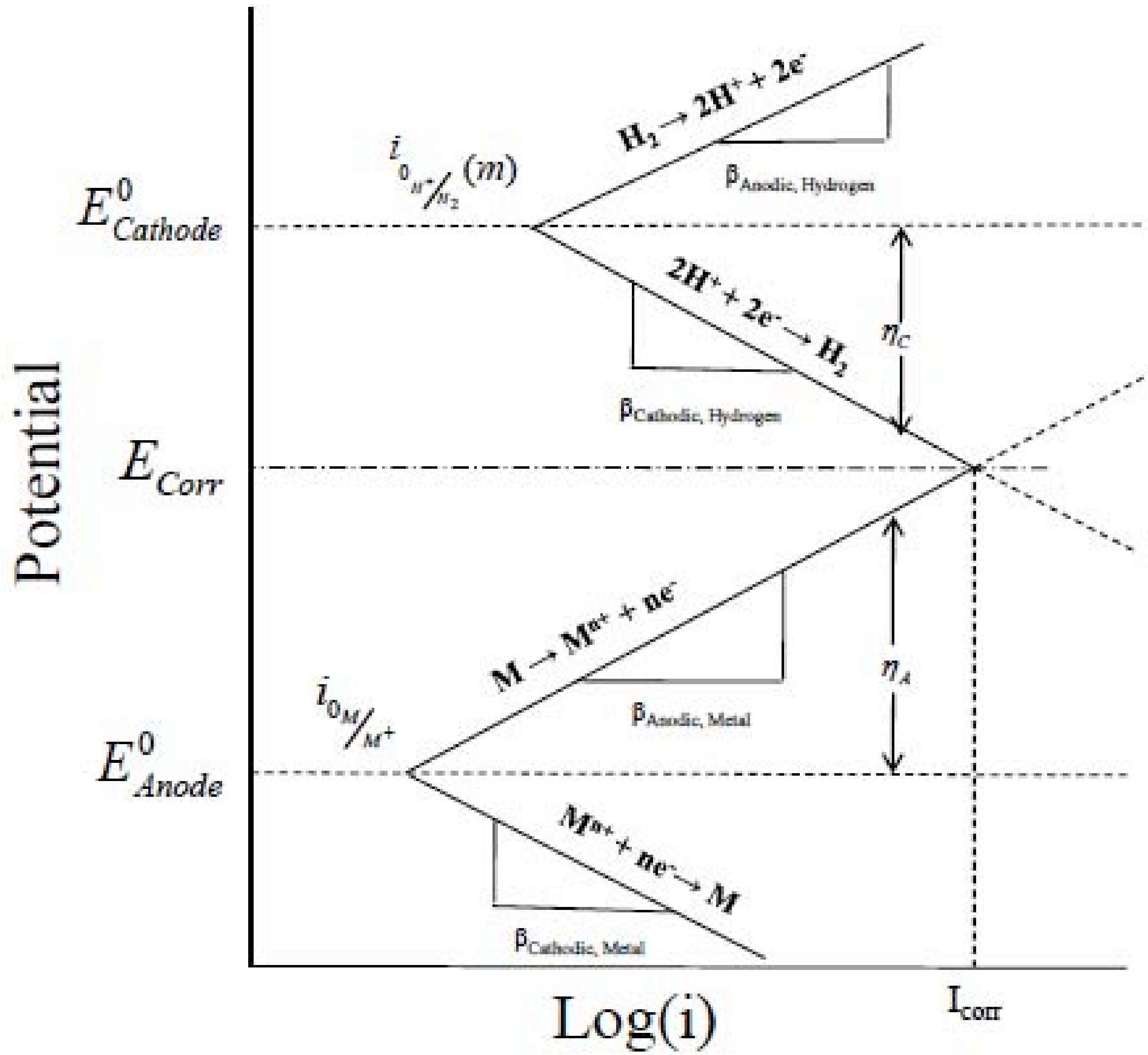
Polarization diagram



$$\eta_c = \beta_c \log \frac{i}{i_0}$$

$$\eta_A = \beta_A \log \frac{i}{i_0}$$

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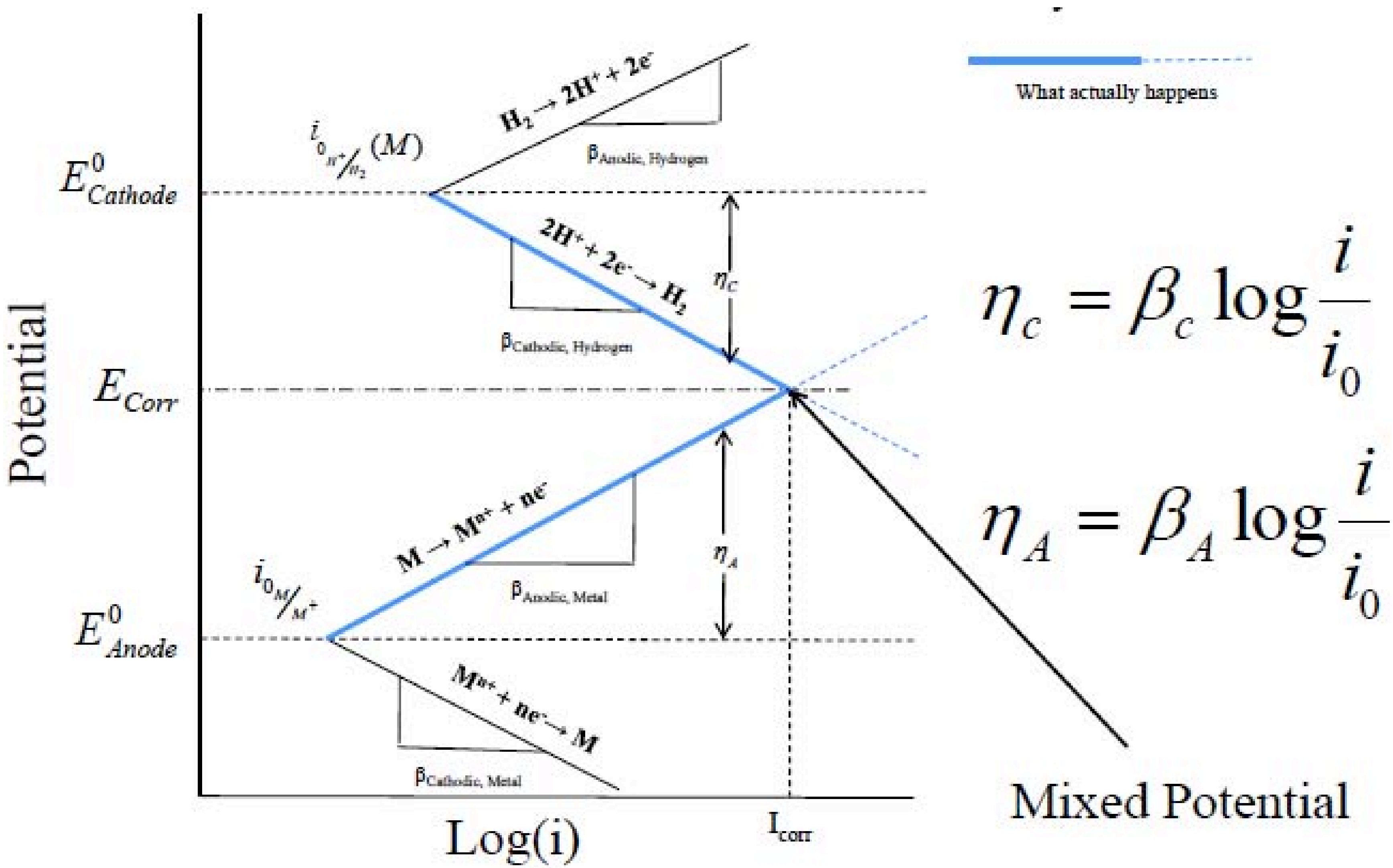
Establishment of a "mixed" potential



$$\eta_C = \beta_C \log \frac{i}{i_0}$$

$$\eta_A = \beta_A \log \frac{i}{i_0}$$

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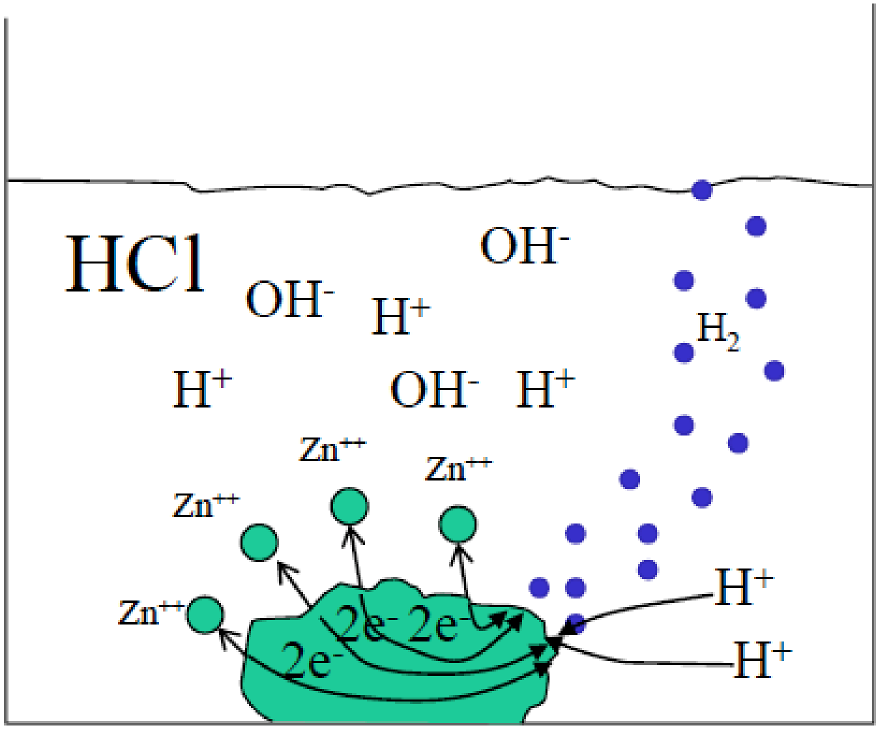
Back to Zinc in Acid solution



Drop a piece of Zn Metal into 1M HCl

Zinc goes into solution (Oxidation-Anode)

$$Zn \Rightarrow Zn^{++} + 2e^{-}$$

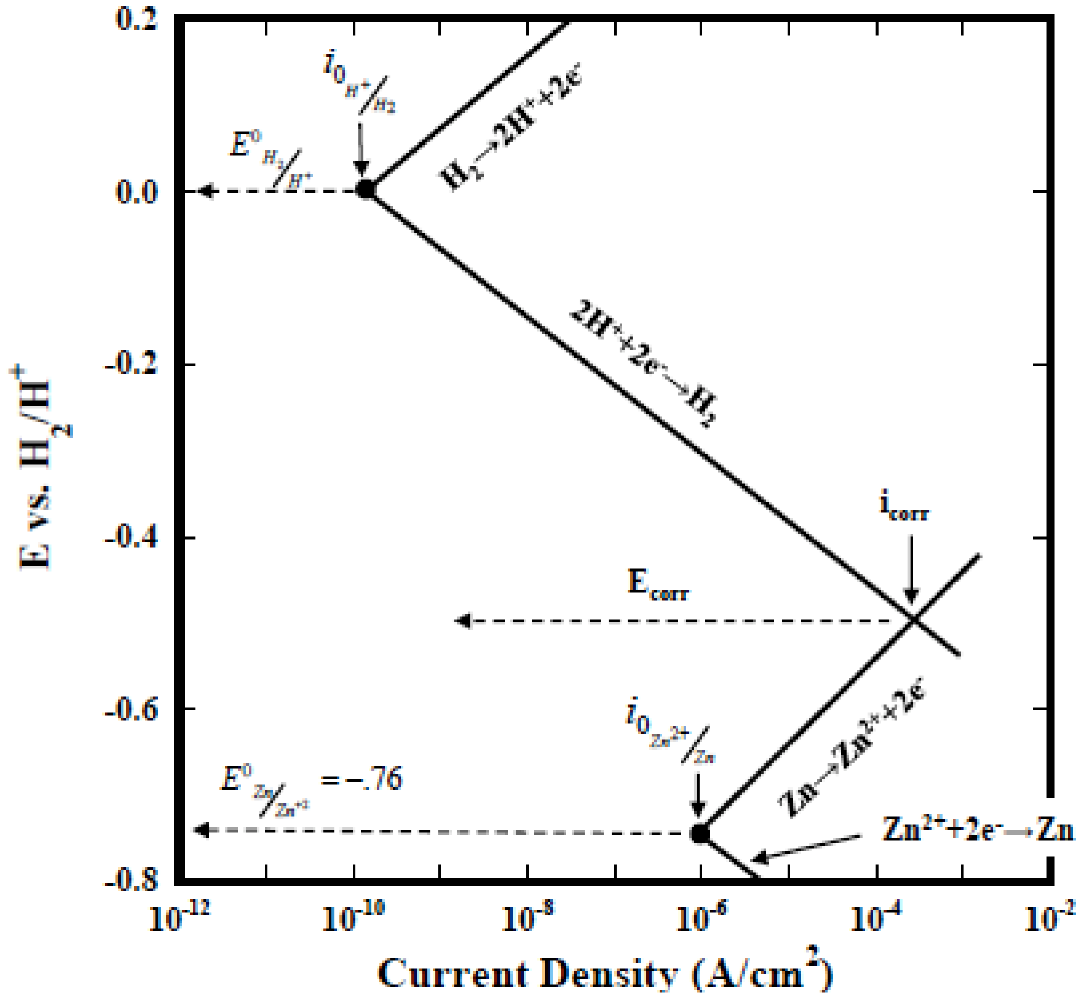
Hydrogen gas is released (Reduction-Cathode)

$$2H^{+} + 2e^{-} \Rightarrow H_2(gas)$$

Note: Electrons are released by oxidation of Zn and consumed by hydrogen Reduction-Charge cannot be stored.

$$\sum_A = \sum_C$$

Polarization diagram for zinc in acid solution

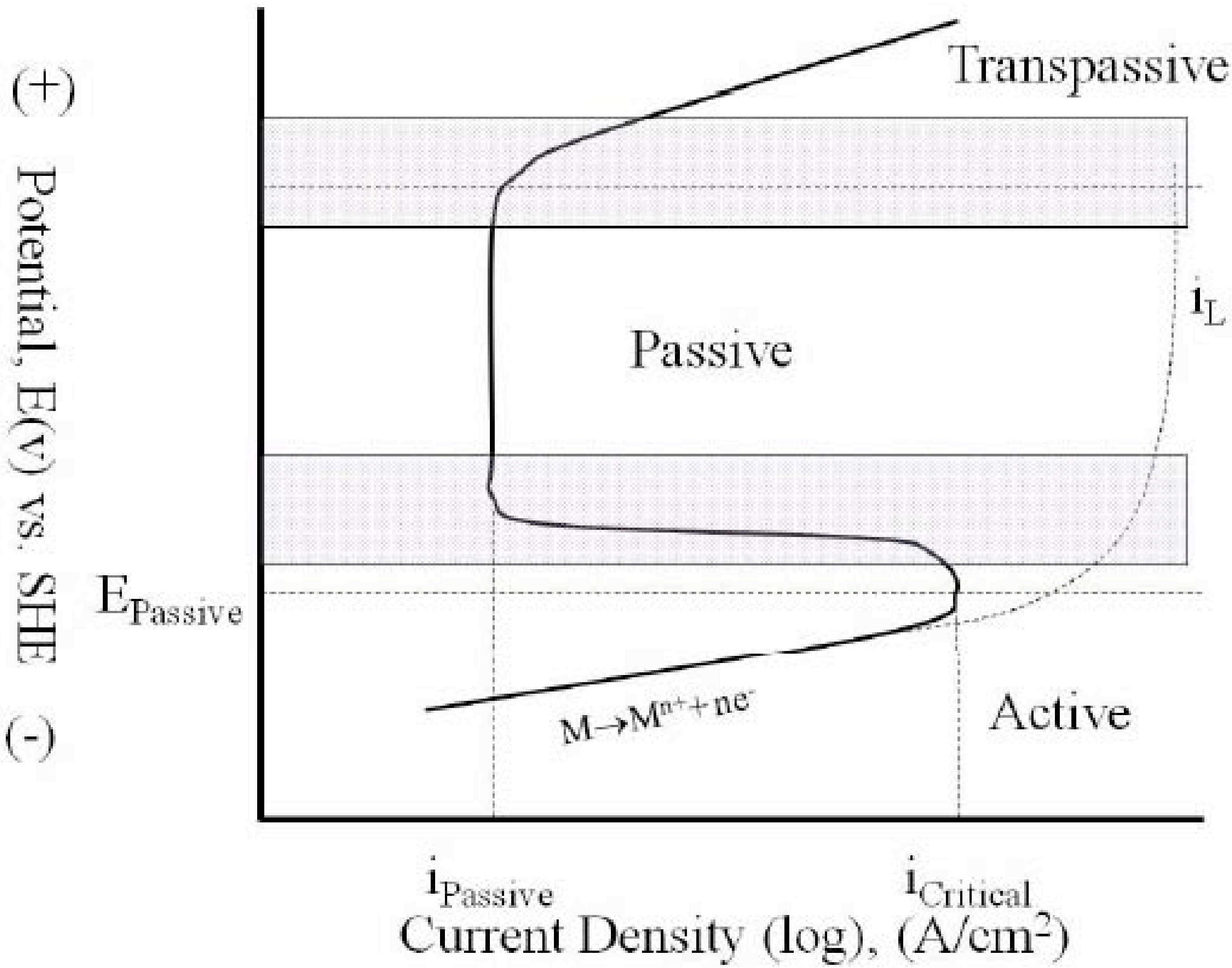


Courtesy Pierre Combrade

Passivation

- A metal is passive if it substantially resists corrosion in a given environment resulting from marked polarization
  - Cr, Ni, Mo, Ti, Zr, Stainless Steels
- A metal is passive if it substantially resists corrosion in a given environment despite a marked thermodynamic tendency to react.
  - Pb/H_2SO_4, Mg/H_2O

Passivation



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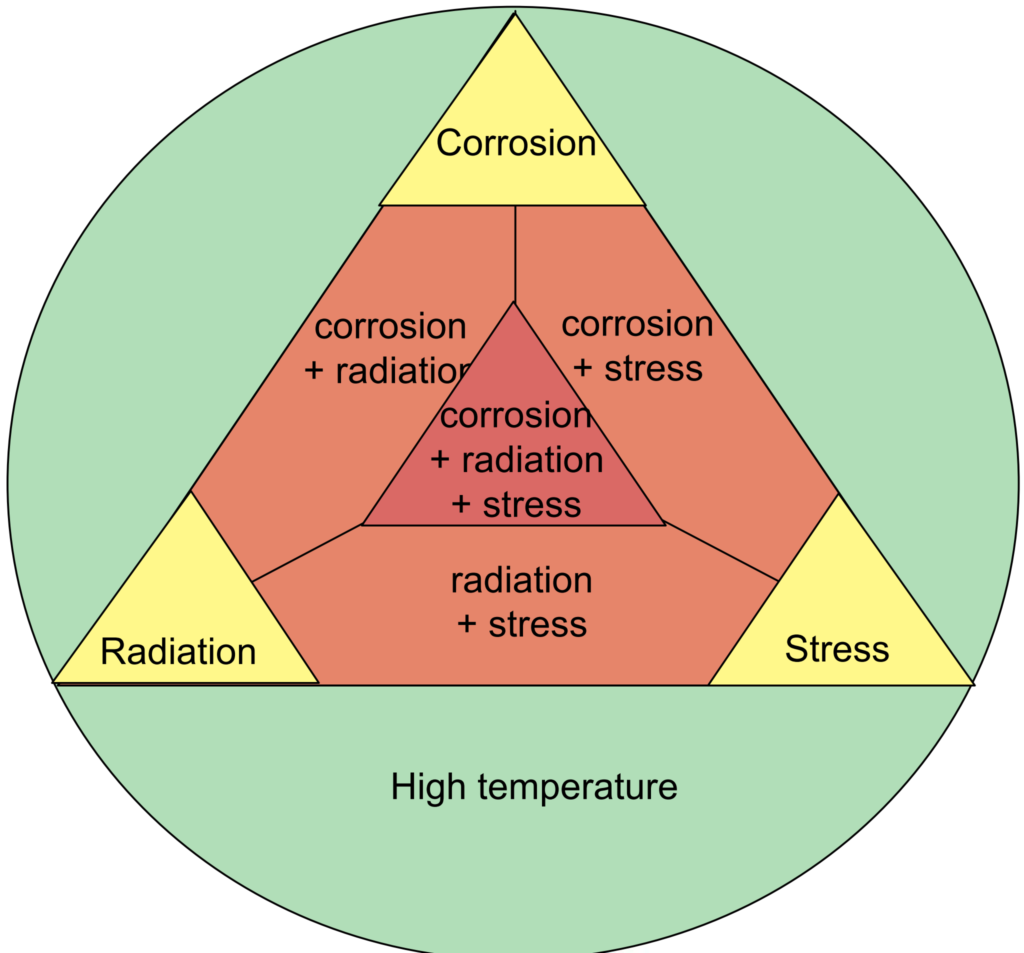
Elements of the environment relevant to nuclear reactor systems

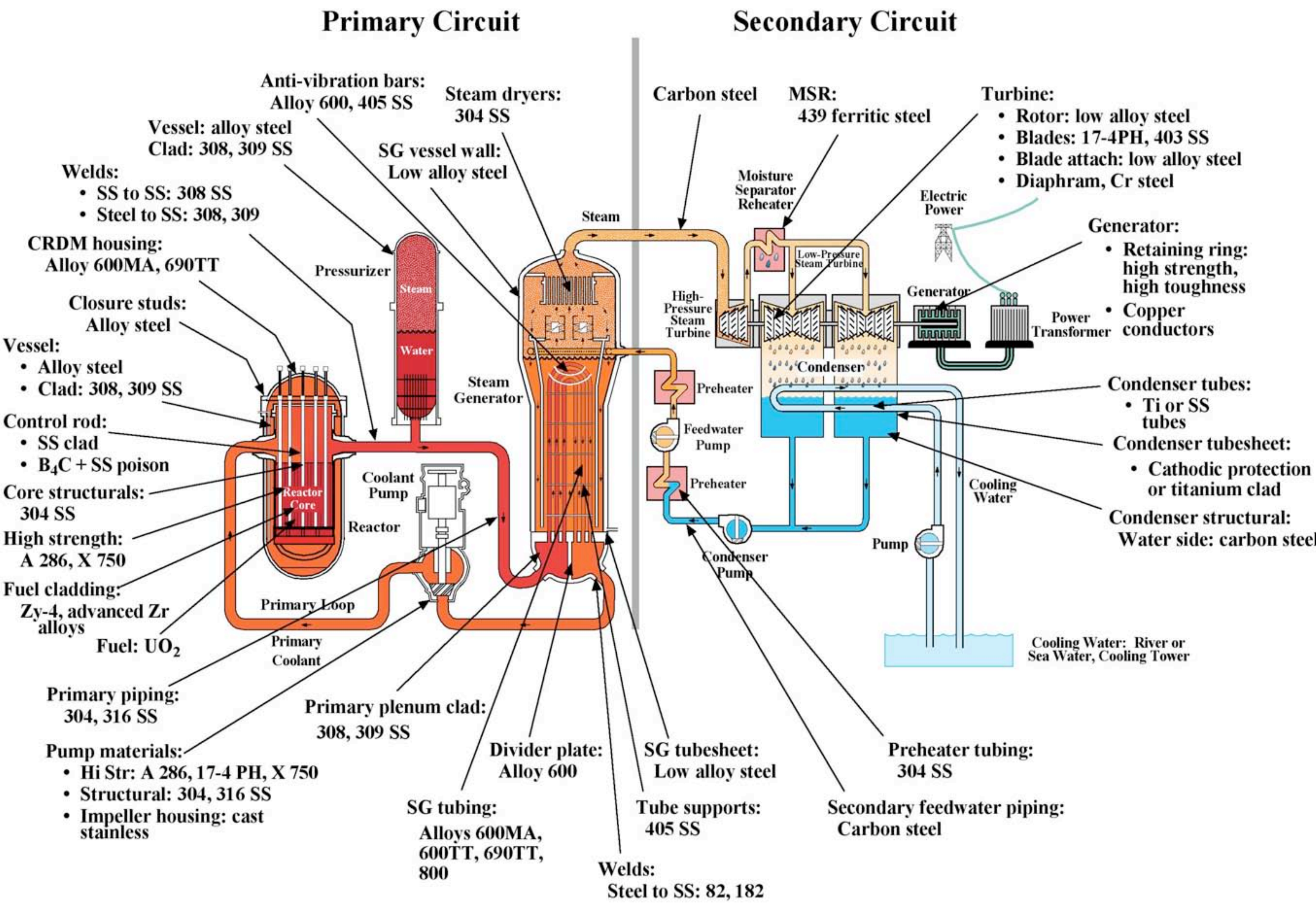
- Temperature
- Stress/Pressure
- Corrosive medium
- Radiation

Elements of the environment relevant to nuclear reactor systems



Materials in Reactor Components

PWR Components and Materials



Principles of Materials Selection for LWRs

Requirements

Ability to manufacture large size components ,

- Hardenability and metallurgical homogeneity,
- Weldability,
- Avoid any significant fabrication defect (cast, welds, underclad…)
- Control (NDT).

Long life (40-60 years) in specific environment :

- Neutron irradiation :
  - Embrittlement
  - Activation of species
- Temperature ~300°C : Thermal Ageing
- Environment : Primary Water, Secondary : Corrosions

Consequences

- Use commercial grades well known by the manufacturers : mainly steels
- Optimize these grades to get :
  - Good resistance to fast fracture (level of impurities : S, P, Cu…, Toughness, RTNDT< -20°C…)
  - Corrosion resistance to reduce release of activated corrosion products

Courtesy J. P. Massoud

Material Property requirements for PWR components

Material Property	RPV	Internals	Pressurizer	Primary Piping	Pump casing	SG Tubes	Secondary Piping
Toughness	x	(x)	x	x	x	x	x
Hardenability	x		x				
Material Homogeneity	x		x	x	x		
Weldability	x		x	x	x	x	x
Corrosion Resistance	x	x	x	x	x	x	x
Irradiation Resistance	x	x					

Courtesy J. P. Massoud

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Summary of Major Materials in PWR

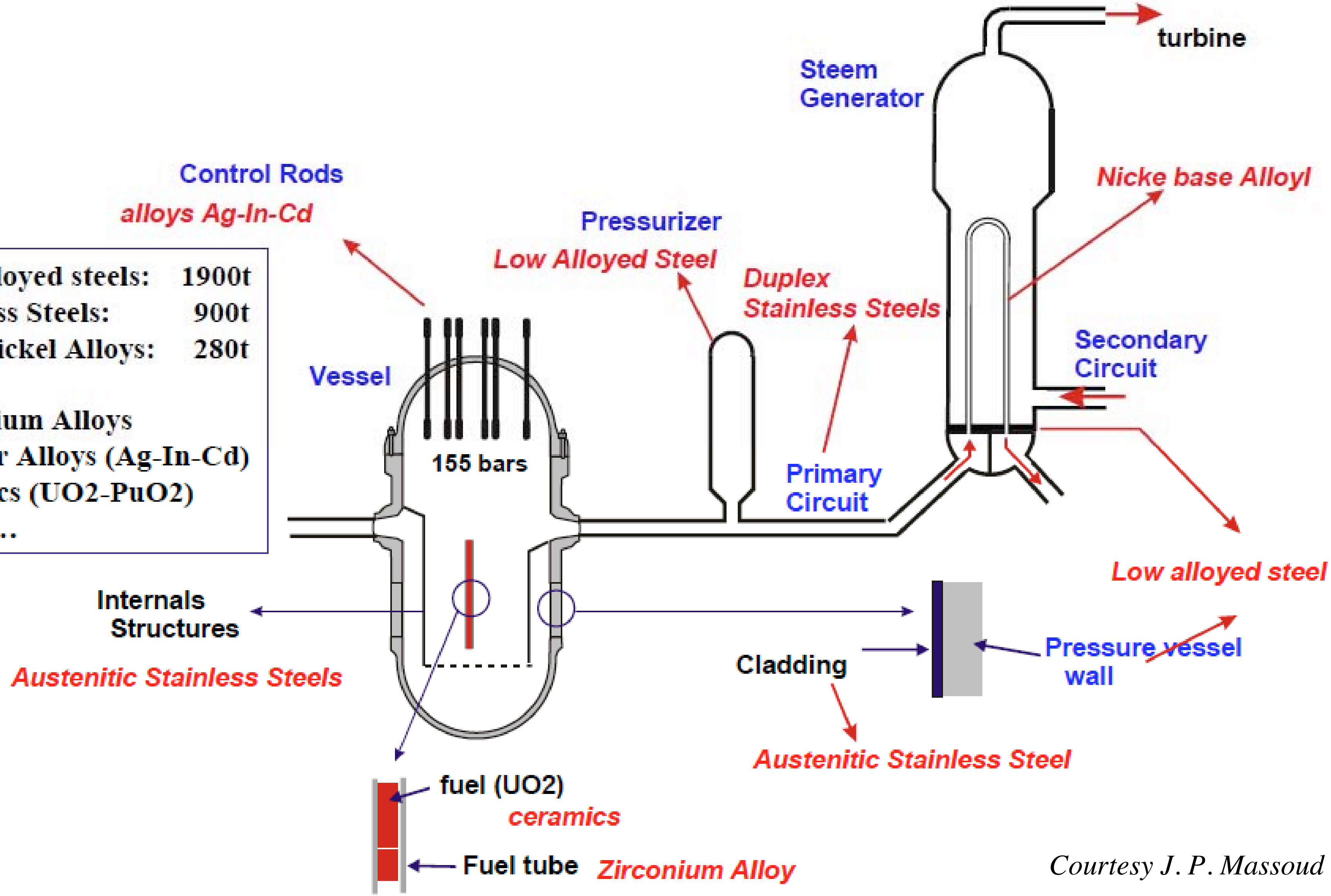
	Carbon Steels	Low-Alloy Steel	Stainless Steel	Ni-Alloys
Cristal structure	BCC	BCC	FCC	FCC
Microstructure	Ferritic, Bainitic	Ferritic, Bainitic	Austenitic	Austenitic
Main alloying elements	0.5-1.5%Mn, Si… Total (out of Ni) < 1%	Mn, Ni, Mo, Cr … Total < 5%	~18% Cr, ~10% Ni	~15% Cr, ~10% Fe ~30% Cr, ~10% Fe
Price	low	low	high	Very high (Ni base)
Grades	TU, A-48 ; TU, A-42, 20MN5M, A106, A333, A515…	16MND5 , A533 Cl.1, A508 Cl.2/3, …	304 (L), 316 (L) Welds : 308L, 309L CF3M, CF8M….	Alloy 600/182/82 Alloy 690/152/52 X750….
Fabrication	Forged, Rolled or cast (valves…)	Forged or rolled and cladded	Forged , Rolled or cast	Forged , Rolled
Heat Treatment	Austenitizing + air cooling	Quenched + tempered + post-weld HT	Solution Annealed (SA) (+ cold work)	Mill annealed Thermally Treated
Yield Strength	250-450 MPa	250-450 MPa	~200 MPa (SA) if CW, YS increases	~300 MPa (SA) if CW, YS increase
Toughness/ductility	High, DBTT	High DBTT	Very high No DBTT	Very high No DBTT
Irradiation resistance	N/A	Moder. (%Cu, P low)	High	High
Corrosion resistance	Risk for FAC	moderate	high	high
		Vessel,	**Primary Piping,**	**SG Tubing, Divider**

Courtesy J. P. Massoud

PWR Components & Materials

- Low alloyed steels: 1900t
- Stainless Steels: 900t
- Base Nickel Alloys: 280t

- Zirconium Alloys
- Nuclear Alloys (Ag-In-Cd)
- Ceramics (UO2-PuO2)
- Cu, Ti…



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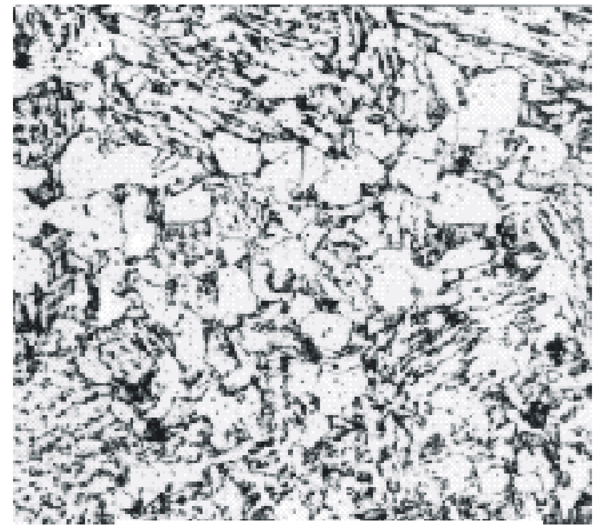
Low Alloy Steels: Reasons for selecting and risks

• Fine-grained structural steels with bainitic microstructure and high toughness.



Ferrite-Bainite Steel 16MND5 (ASTM 508)

• Hardenability and materials homogeneity: Balance Mn, Ni, Mo, Cr…

• Toughness: S< 0,010%, S , toughness

• Risk of ageing : shift of DBTT (fracture toughness decrease)
  - Irradiation embrittlement: low Cu (Cu < 0.05%) and low P content
  - Thermal ageing : low P content

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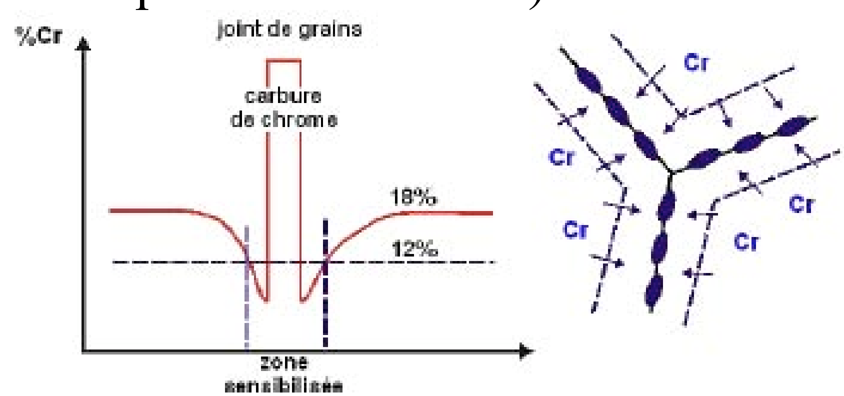
Austenitic Stainless Steels: Reasons for selecting and risks

- Effect of alloying elements:
  - Cr% for general corrosion resistance
  - Ni% for austenite phase stability
  - C and N% for strength and austenite stability

- Nonmagnetic, good weldability (%B low), easy forming (forging, cast)…

- Risk of Intergranular Corrosion (due to chromium depletion at carbides)
  - Low carbon SS (304L)
  - Ti or Nb stabilized grade (321 or 347)



- SS weld materials designed to have 5-10% d-ferrite to avoid hot cracking

- Cast stainless steels CF3M and CF8M also 5-20% d-ferrite,
  → Risk of thermal ageing: ferrite as low as possible

Courtesy J. P. Massoud

Nickel Base Alloys : Reasons for selecting and risks

- Good general corrosion resistance (low corrosion products release rates)
- Resistance to chloride cracking (secondary side)
- Similar thermal expansion coefficients with LAS
- PWSCC of Alloy 600 → Alloy 690

Courtesy J. P. Massoud

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Welds and Claddings

• Welds and Heat Affected Zones are critical components locations (defects, residual stresses, NDT),

• Homogeneous welds : SS to SS (ferrite content), LAS to LAS

• Dissimilar welds : LAS to SS or LAS to A600 (A690)
  - Different chemical compositions : Dilutions
  - Different thermal expansion coefficients : Thermal stresses

• Heat Affected Zones (HAZ) :

• Weld Defects : Hot cracking, lack of fusion, weld roots defects, relaxation cracking, excessive dilution (low ferrite content or martensite in SS welds

Courtesy J. P. Massoud

Zirconium Alloys

- Very low neutron absorption cross section

- Very poor corrosion resistance as a pure metal, but can be alloyed to produce good corrosion resistance

- Susceptible to I-induced SCC (I is a fission product)

- Zr has an hcp structure, so it is highly anisotropic
  - susceptible to radiation induced hardening
  - radiation induced growth
  - radiation induced creep

Courtesy J. P. Massoud

Environments of Reactor Components

PWR Water Chemistries

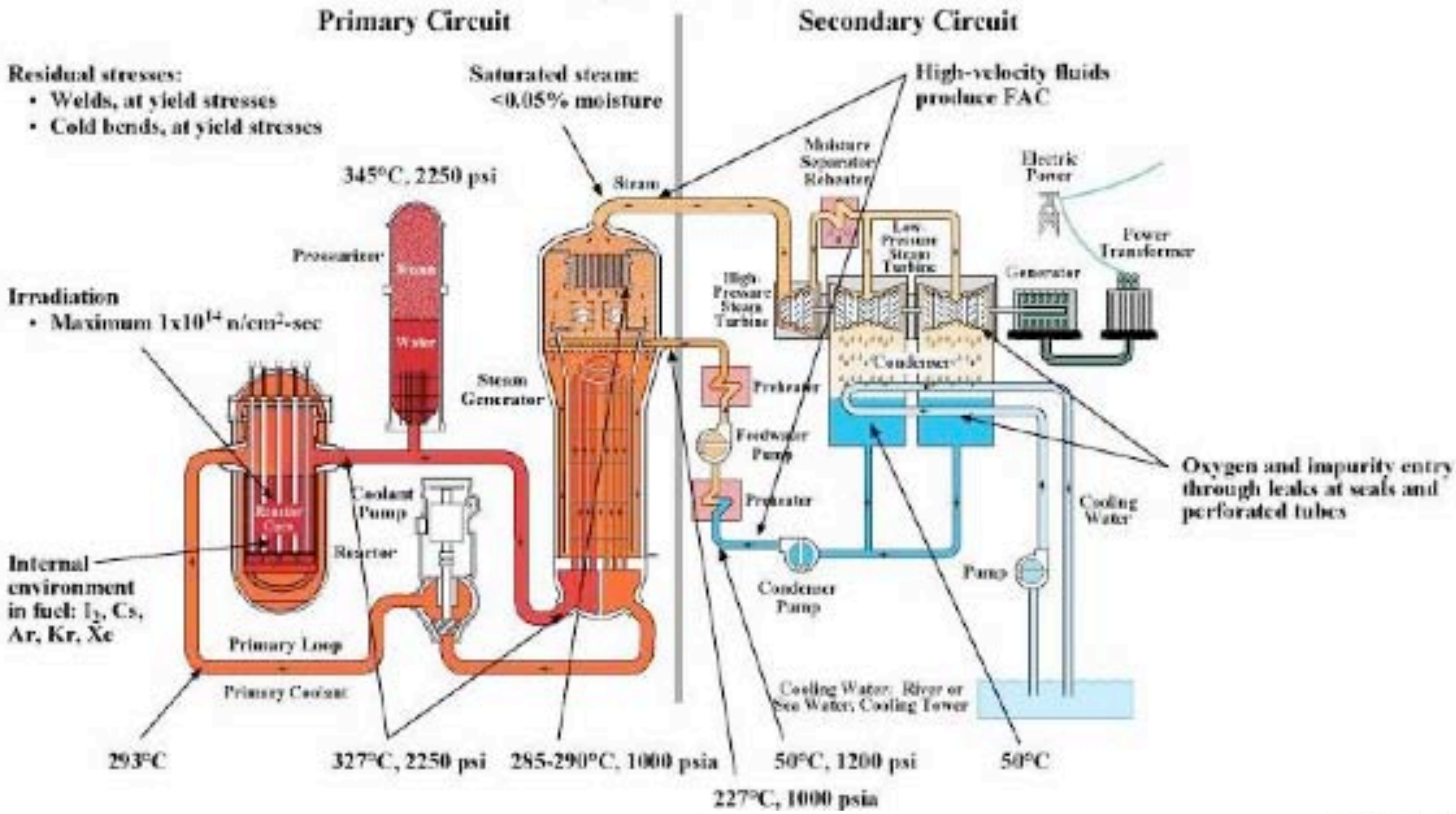
Primary Water Chemistry

Role	Species	Concentration
Burnable poison	H_3BO_3	1500 ppm to zero
pH adjust	LiOH	Adjust to meet 7.1-7.4 pH_T
Minimize radiolytic oxygen	H_2	25-50 STP cc/kg
Oxygen	O_2	< 5 ppb
Corrosion product	Fe, Ni, Co	No spec.
Contaminant	Cl, SO_4, F	Each < 0.15 ppb

Secondary Water Chemistry

Role	Species	Conc., ppb
pH control	NH_3	~ X
O_2 decrease	N_2H_4	$\leq 8xO_2$
Leaks	O_2	< 10
Boil off remnant	H_2	~ 1
Corrosion product	Cu	< 1
	Fe	< 5
Contaminant	Na	< 5
	Cl_2	< 10
	SO_4	< 10

Bulk PWR Environments:
Water Chemistry, Stress, Thermal, Radiation



Primary water chemistry

- avoid water radiolysis via low corrosion potential
- minimize oxidation of zirconium clad
- minimize activity of circuit
- minimize crud deposition on fuel

Source: P. Combrade

	Typical
Pressure (MPa)	14.2
Temperature (°C)	286-323
Oxygen (ppm)	<0.1
Conductivity ($\mu S.cm^{-1}$)	1-40
Hydrogen (ml/kg) at STP	20-50
Lithium (ppm) as LiOH	0.1-3.5
Boron (ppm) as H_3BO_3	0-2300
Chloride (ppm)	<0.15
Fluoride (ppm)	<0.15
SiO_2 (ppm)	<0.20
pH_T	6.8-7.4

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Water chemistry in PWR primary circuit

Pressure

- high enough to avoid boiling
- local boiling may occur and cause formation of deposits that lead to axial offset anomaly (AOA)

Boric acid

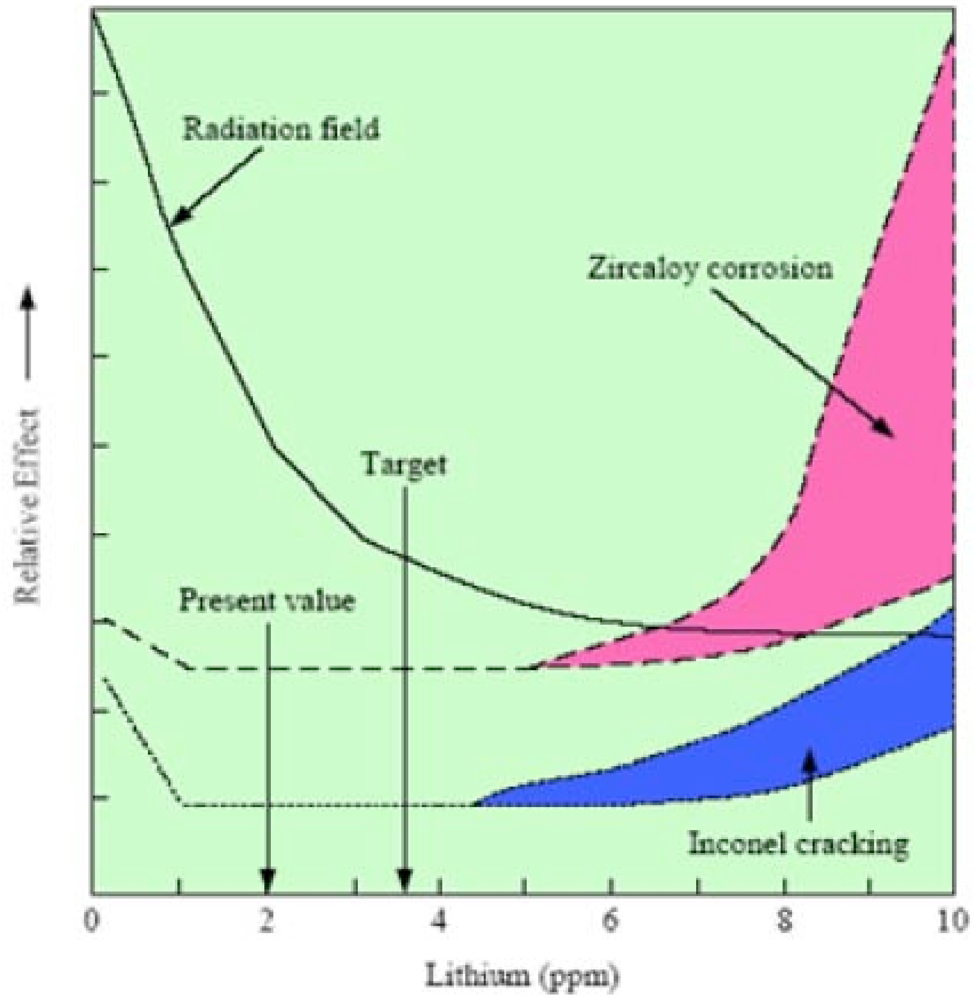
- controls nuclear reaction
- decreases throughout fuel cycle

Lithium hydroxide

- to control pH - product of nuclear reaction with B
- conc. from 2.1 -> 3.5 ppm to reduce activity in circuit

Oxygen

- specification is <0.1 ppm
- much lower in service



Source: P. Combrade

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Water chemistry in PWR secondary circuit

- Minimize corrosion problems (SG tubes, C-steel, Cu alloys in condenser tubing)
- Minimize formation of deposits (fouling of tube in free span, blockage of TSPs)
- Minimize costs and waste release

	Typical
Pressure (MPa)	5.4 – 7.2
Temperature (^oC)	284 - 305
Oxygen (ppm)	<0.005
Conductivity ($\mu S.cm^{-1}$)	<0.5
NH_3, morpholine or ethanolamine	As required for pH_T
Hydrazine (ppb)	Initially $[O_2]$+ 5 Now 50 to 100 Or > 20 and > 8X$[O_2]$ (EPRI)
Sodium (ppm)	<0.005
Chloride (ppm)	<0.03
SiO_2 (ppm)	<1
pH_{25}	8.9 - 10

Source: P. Combrade

Operational Experience with Corrosion of Reactor Components

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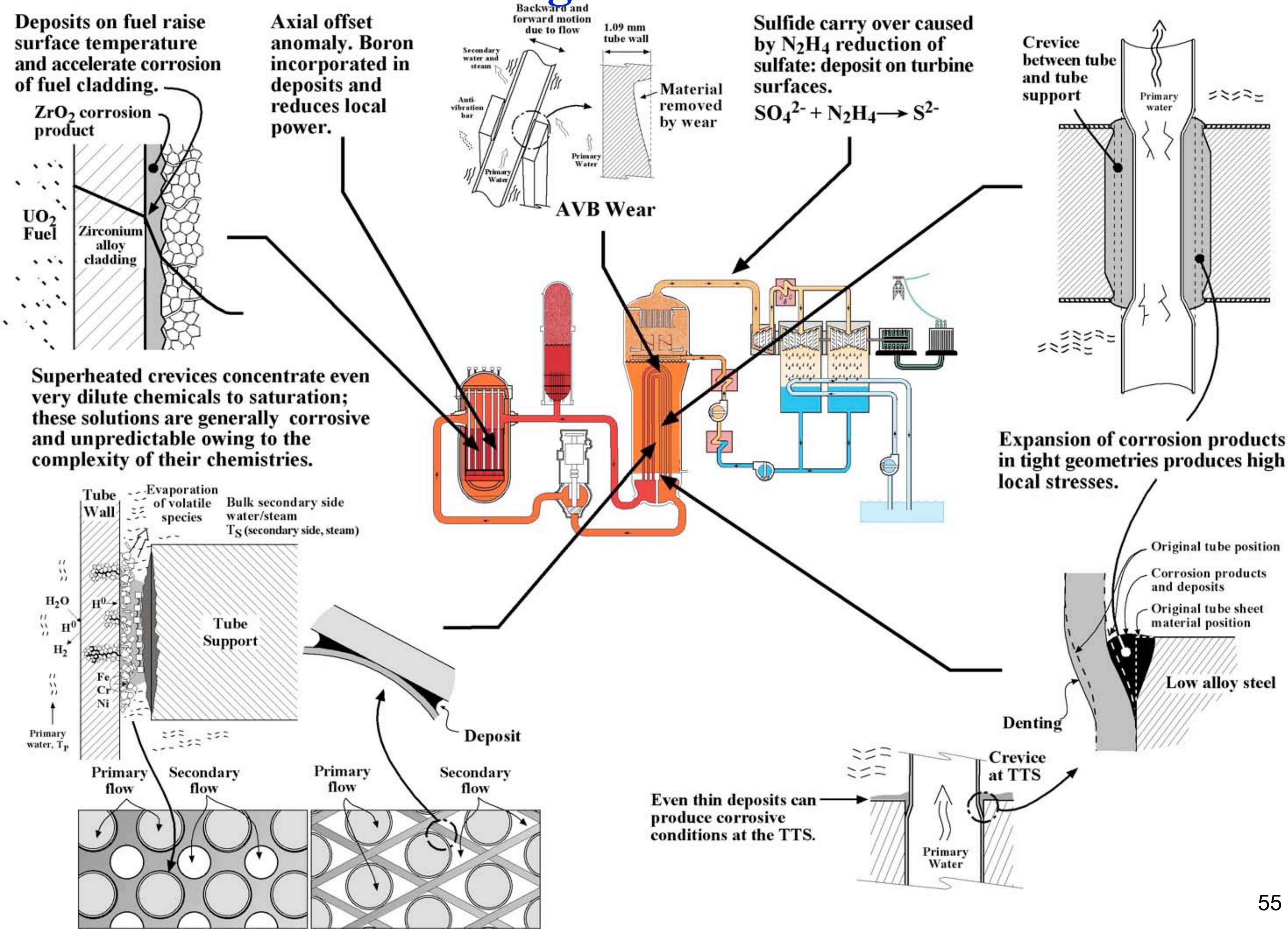
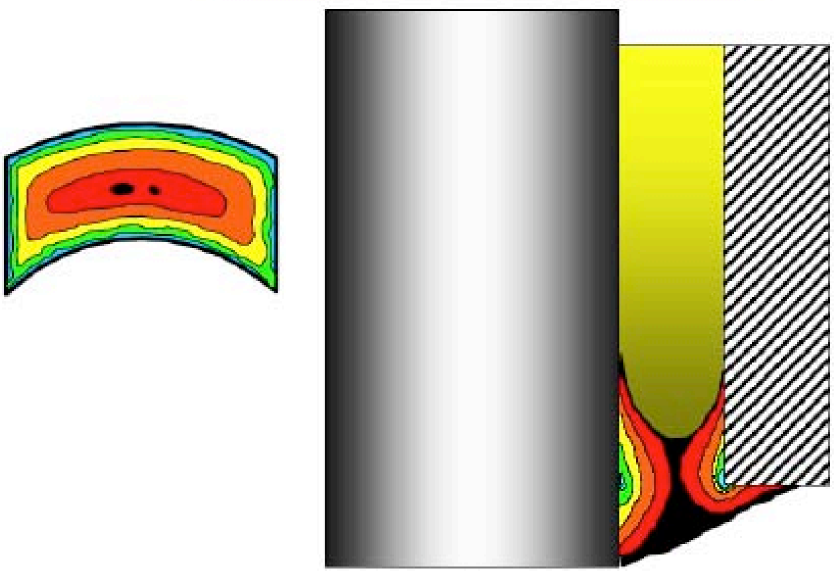
Material degradation in PWRs



Corrosion of SG Broached Tube Support Plates

TSP broached area and typical blockage deposit (after Corredera et al,2008)



Too low a secondary side pH seems to be the main aggravating factor

Courtesy Peter Scott

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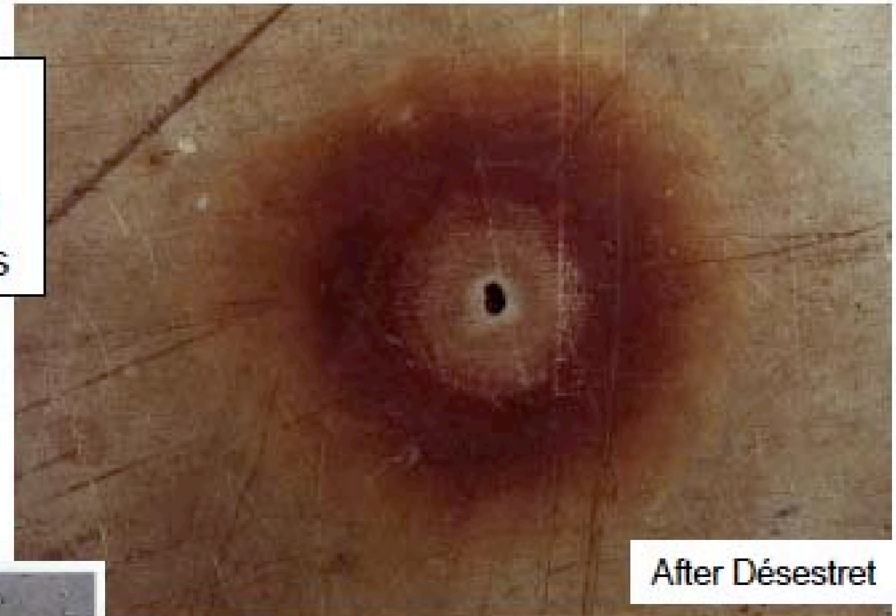
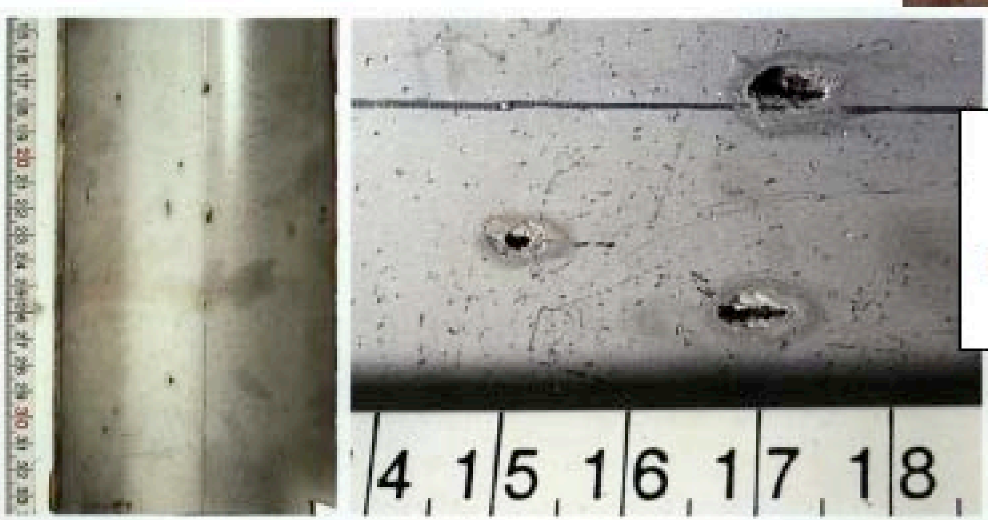
Pitting Corrosion

Type 304 stainless steel pitted in a rinsing solution containing chloride ions and unidentified sulphur species



After Désestret



Type 304 stainless steel in a bromide solution: note the role of scratches on pit initiation

After During

Courtesy Peter Scott

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Crevice Corrosion

Corrosion under a Type 316 stainless steel seal in brackish water (after During)

Corrosion under deposits of a Type 316 L ship tank washed with sea water and inefficiently rinsed (After A. Désestret)

Courtesy Peter Scott

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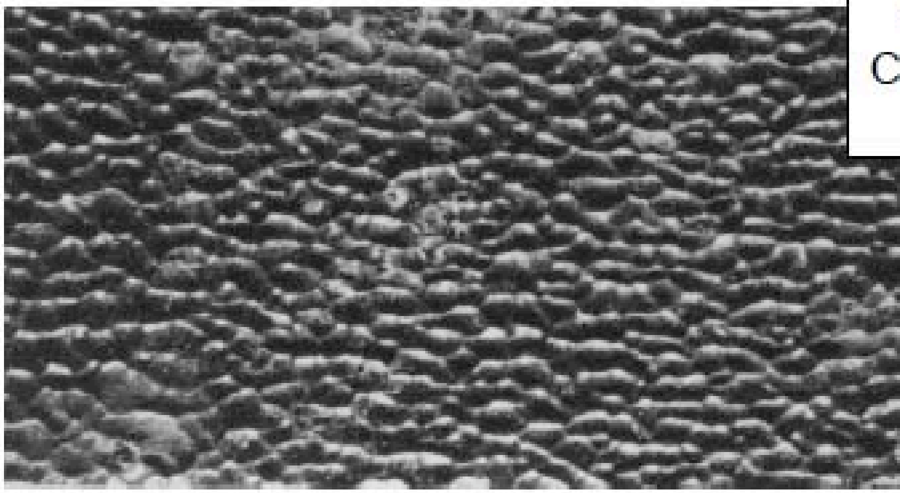
Flow Assisted (Accelerated) Corrosion



Scalloped surface of C-steel in 200 °C water (condensate)

Monel back-pressure control valve of a pump for cooling margarine:
80% Water (pH 4, 8% NaCl), 20% fat, 45 °C
(After During)

Courtesy Peter Scott

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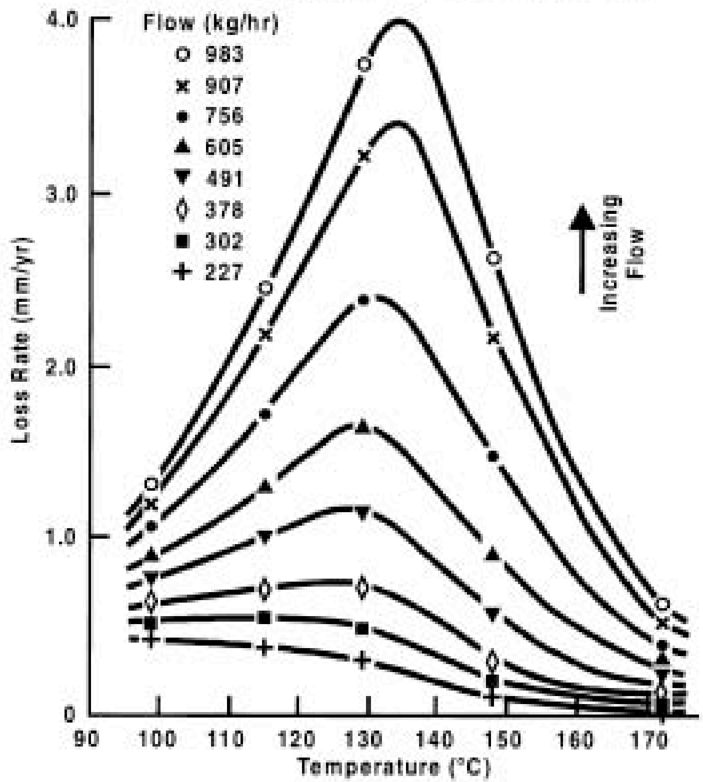
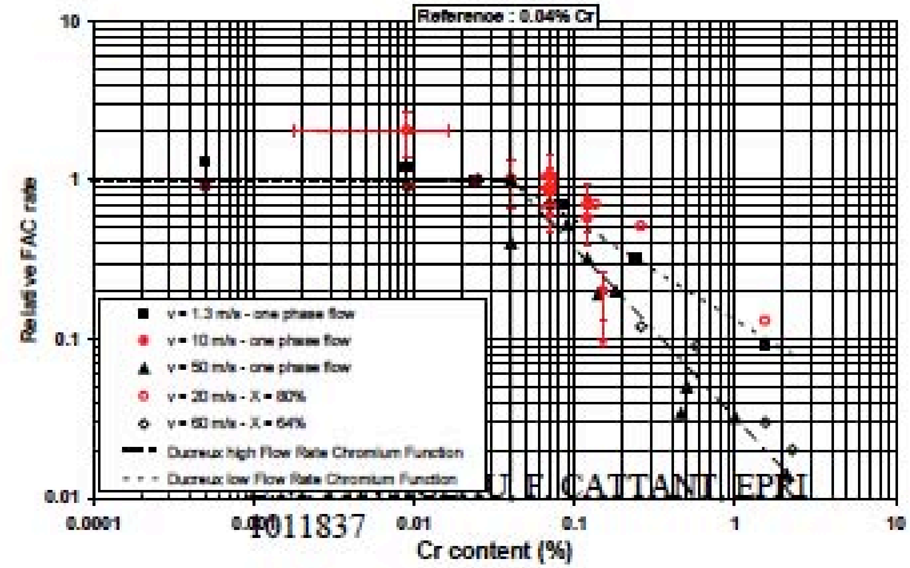
Effect of Flow Rate, Temperature and Chromium Content on FAC Carbon Steel

* Effect of flow rate and T



* Effect of Cr



* Minor effect of N_2H_4

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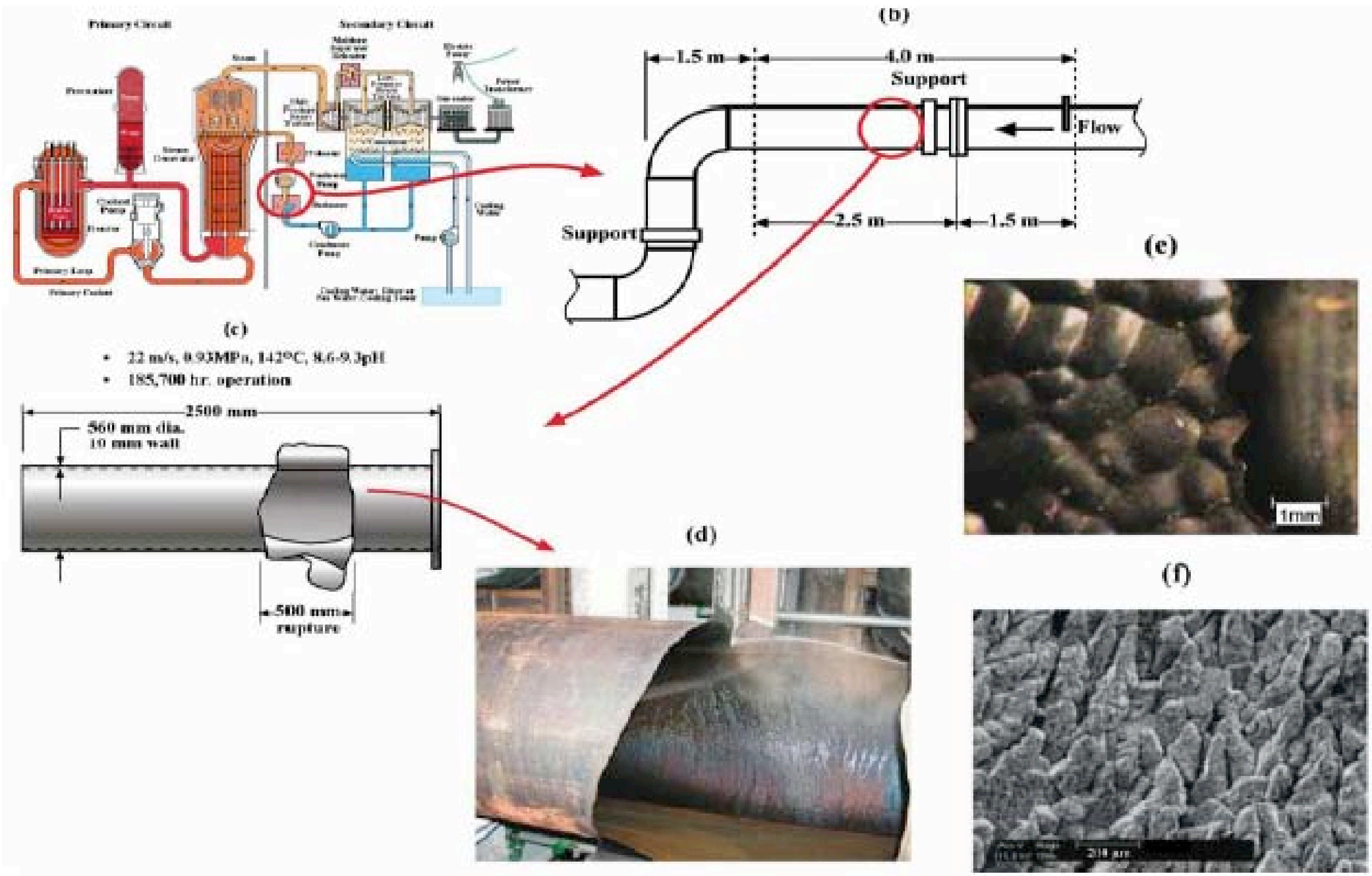
Mihama 3 FAC Incident, 2004



Courtesy Peter Scott

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Erosion Corrosion

- Erosion Corrosion = metal loss due to abrasive particles in the environment

Type 914L Pump rotor
in phosphoric acid
containing solid salt particles:
After a few months of service
(After Audouard)

Duplex Stainless Steel
in natural gas containing particles
of sand and clay
(After During)

Courtesy Peter Scott

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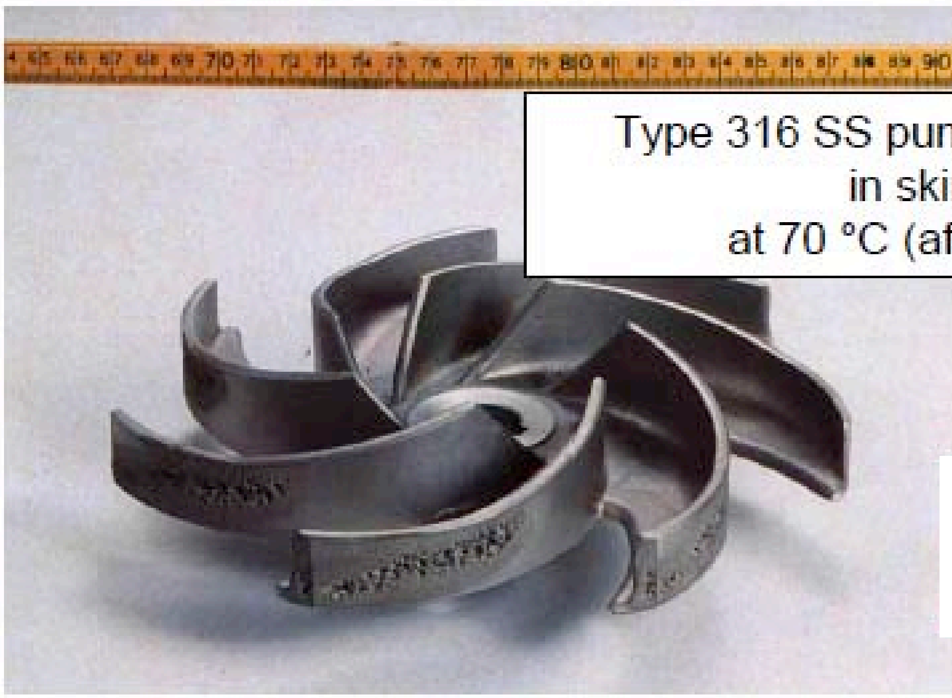
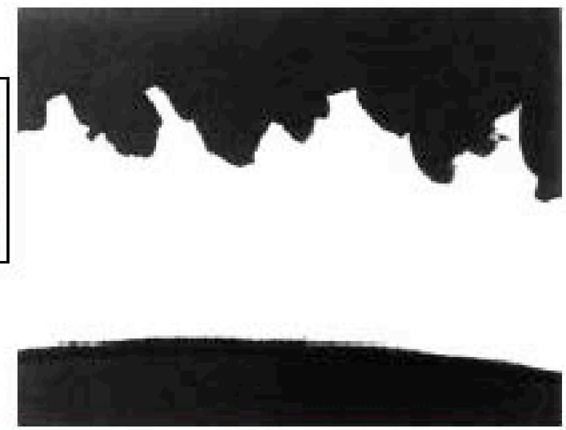
Cavitation-corrosion

- Cavitation-corrosion = mechano-chemical damage due to cavitation (caused by implosion of vapour bubbles) in high turbulent flow
  - Compared to FAC, cavitation corrosion creates ragged surfaces with some surface cold work due to the mechanical effect of cavitation



Type 316 SS pump impeller in skimmed milk at 70 °C (after During)



Courtesy Peter Scott

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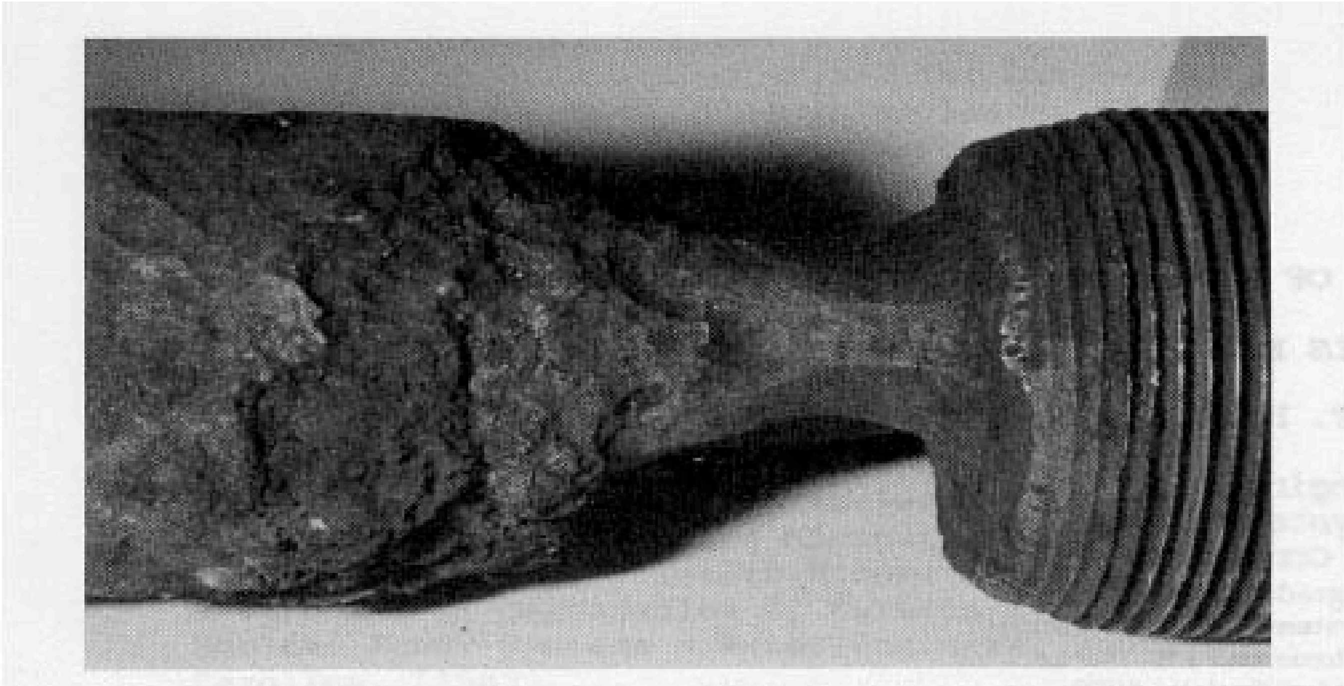
Boric Acid Corrosion of Low Alloy Steel Bolting

- General corrosion by boric acid and steam cutting due to primary water leaks can lead to a severe reduction in shank diameter



Czajkowski, 1983

Courtesy Peter Scott

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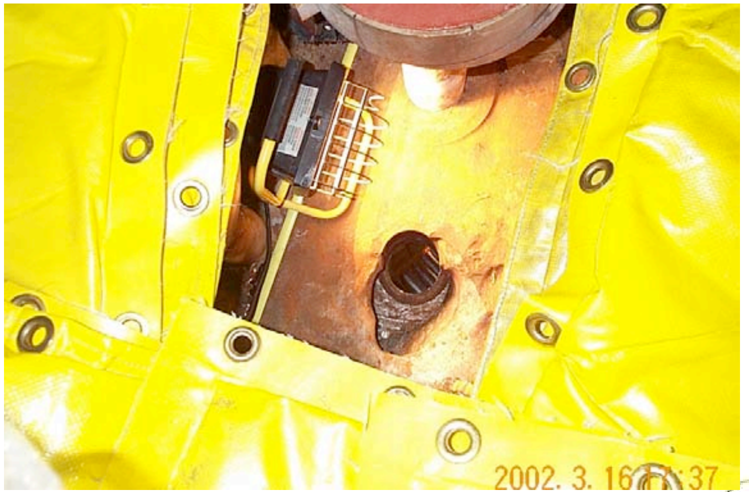
Davis Besse
RPV Head Degradation- Nozzle 3



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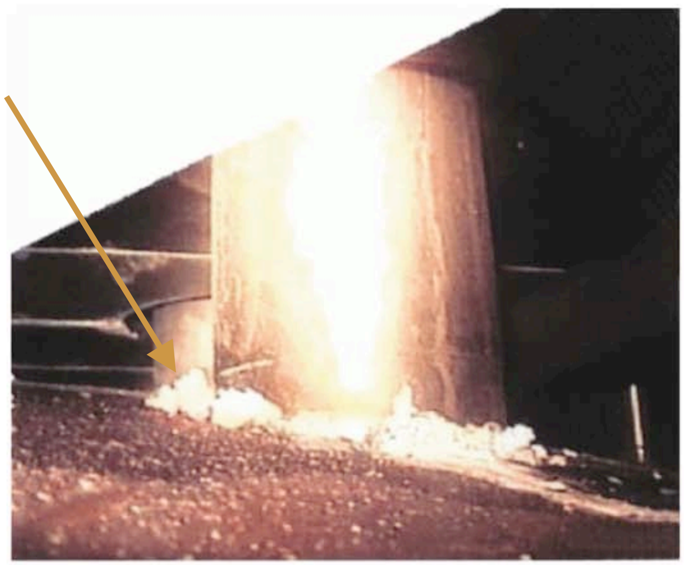
Davis-Besse is not a unique incident

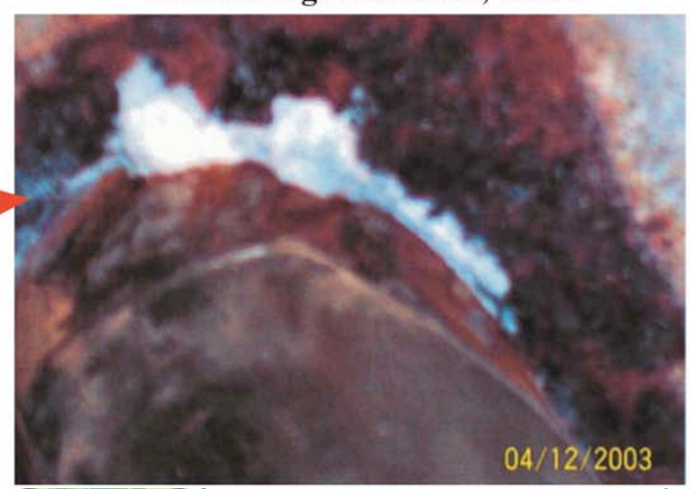
(a)
Oconee, Unit 1



(b)
Oconee, Unit 3

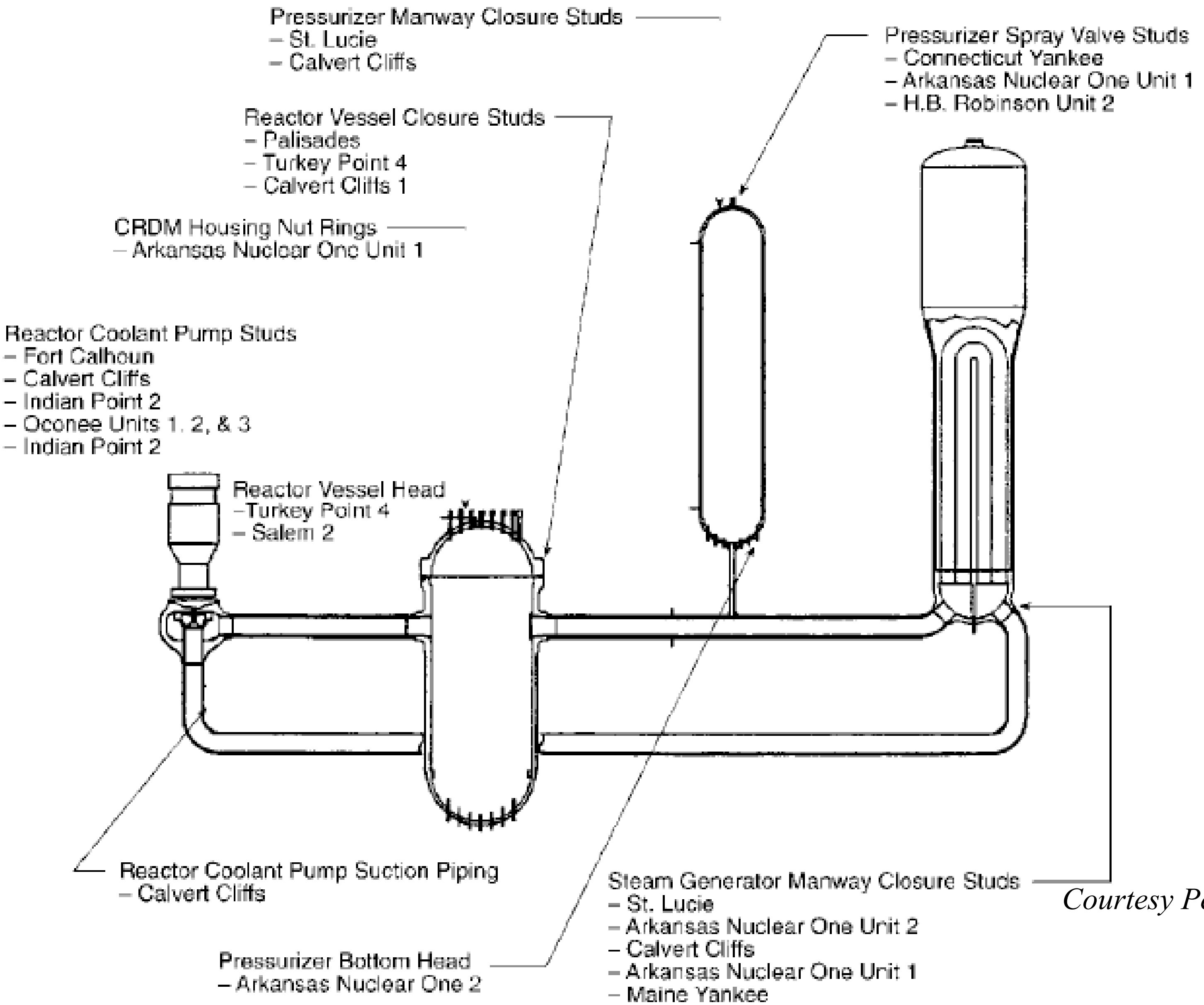
(c)
Houston Light & Power, Unit 1

(d)
Houston Light & Power, Unit 1



Source:
R. Staehle

BAC in US PWR Primary Systems



Courtesy Peter Scott

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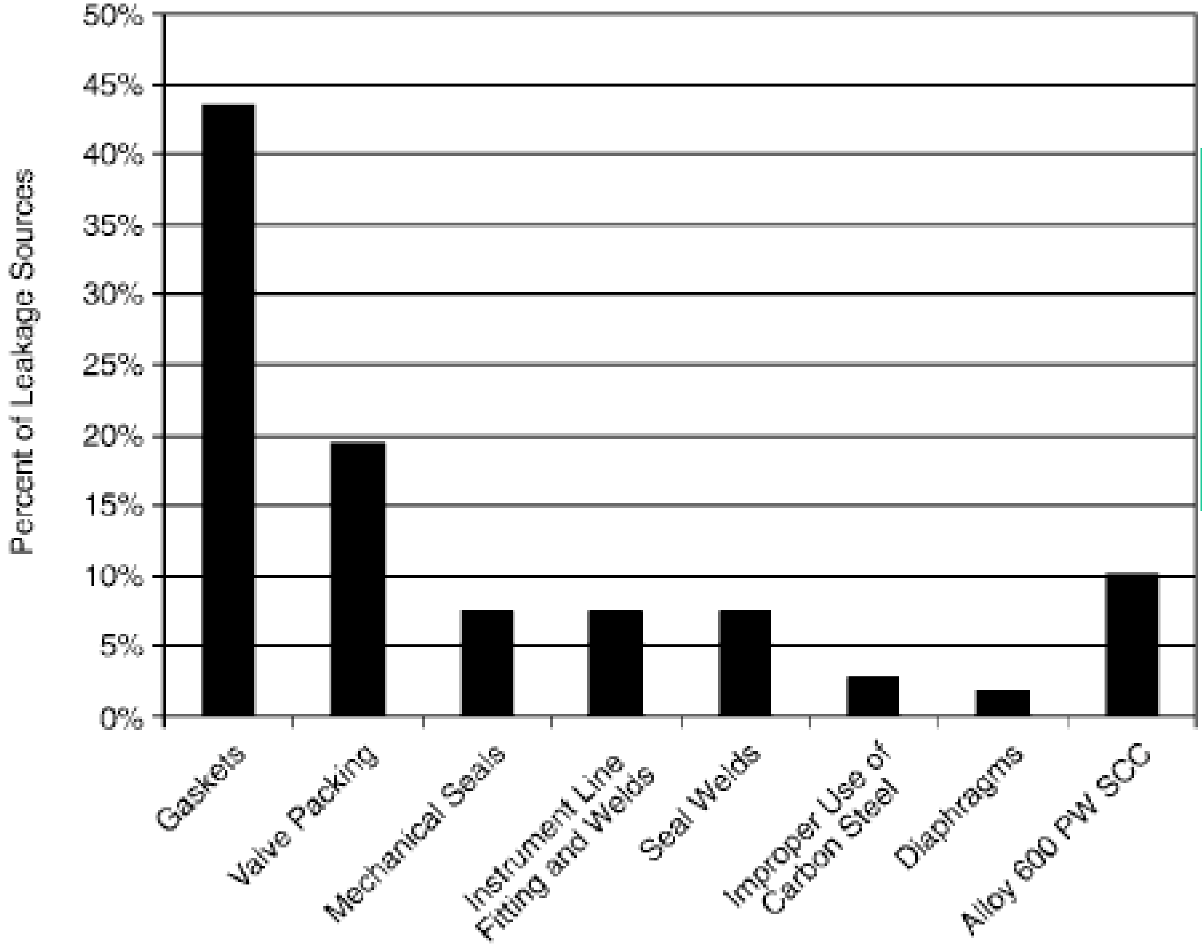
Frequency of BAC as a Function of Location in PWR Systems



Courtesy Peter Scott

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Microbial Corrosion

- Aerobic and anaerobic microorganisms

Duplex weld SS
possibly corroded by SRB

Pit induced by ennoblement
due to Manganese Oxidising
MicroOrganisms (MOMOs)
in low chloride water
(after Linhardt)

Courtesy Peter Scott

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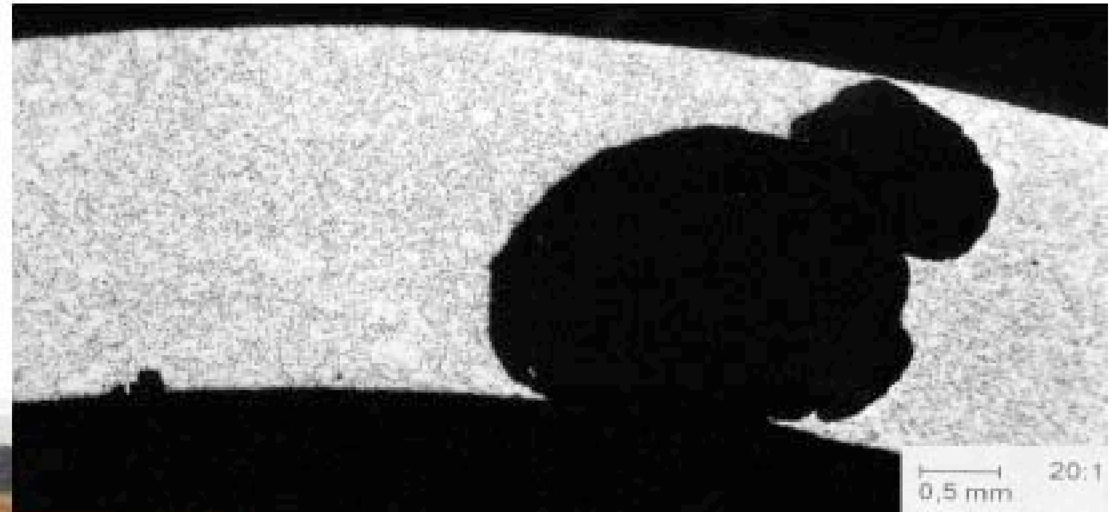
Example of MIC in a FFW-line

(After Maussner, 2006)

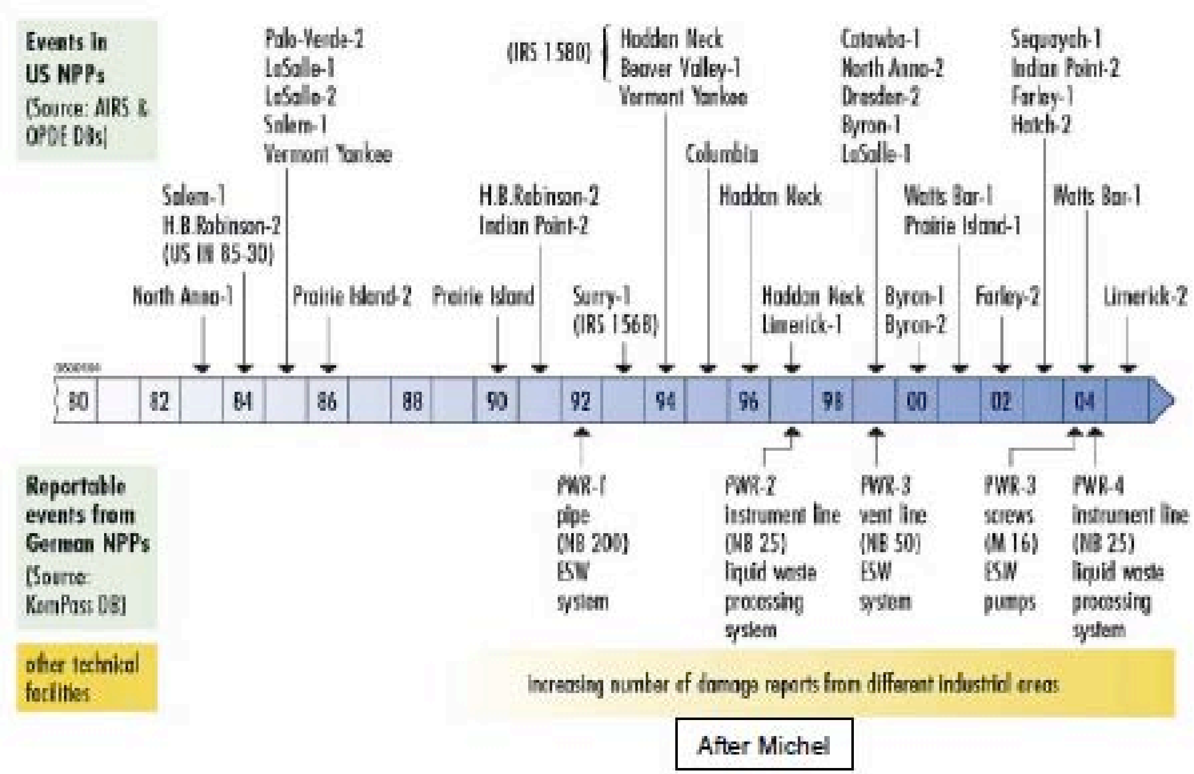


•Perforation after approx. 2 years of operation
•Material: 1.4541 (equivalent to Type 321)
•Medium: Deep well water, drinking water, stagnant
•Temperature: Ambient

Courtesy Peter Scott

MIC in NPPs

- Significant number of events:
  - mainly in auxiliary circuits;
  - some of them involving very large numbers of weldments



Courtesy Peter Scott

Stress Corrosion Cracking

- Cu alloys in presence of ammonia

Coffee pot left during one night in the vicinity of « polluted » baby nappies (After A. Désestret)

Al brass (Cu 2Al Mn) condenser bolt in the presence of traces of ammonia in condensate (after During)

Courtesy Peter Scott

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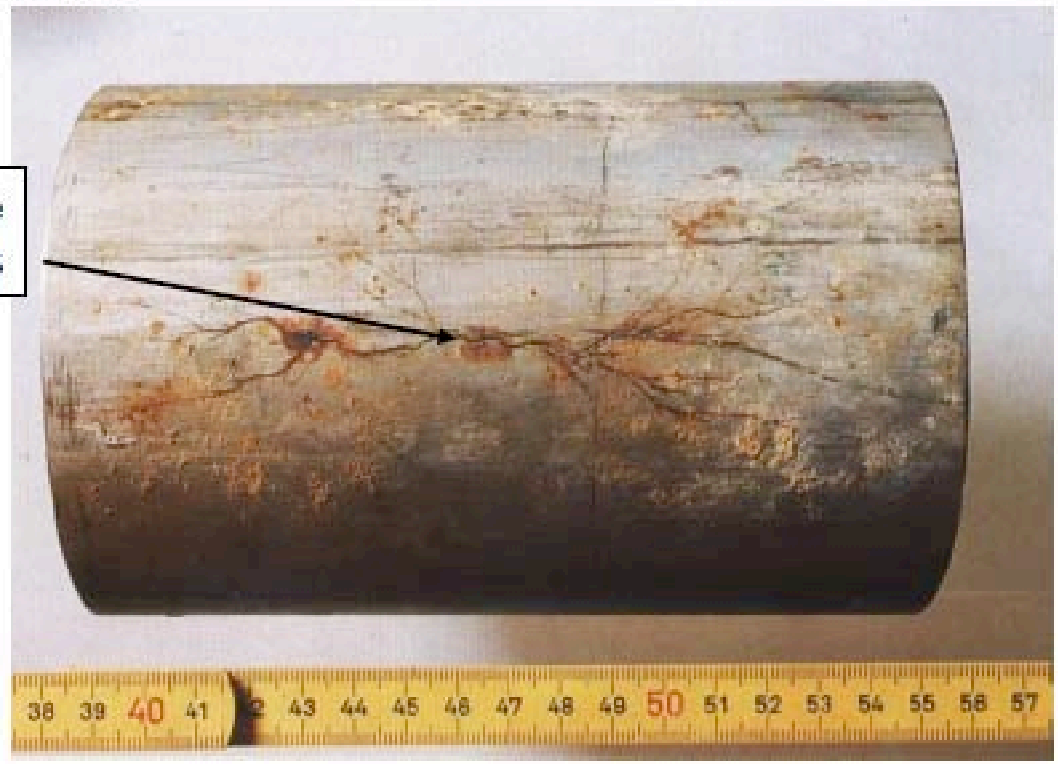
Stress Corrosion Cracking

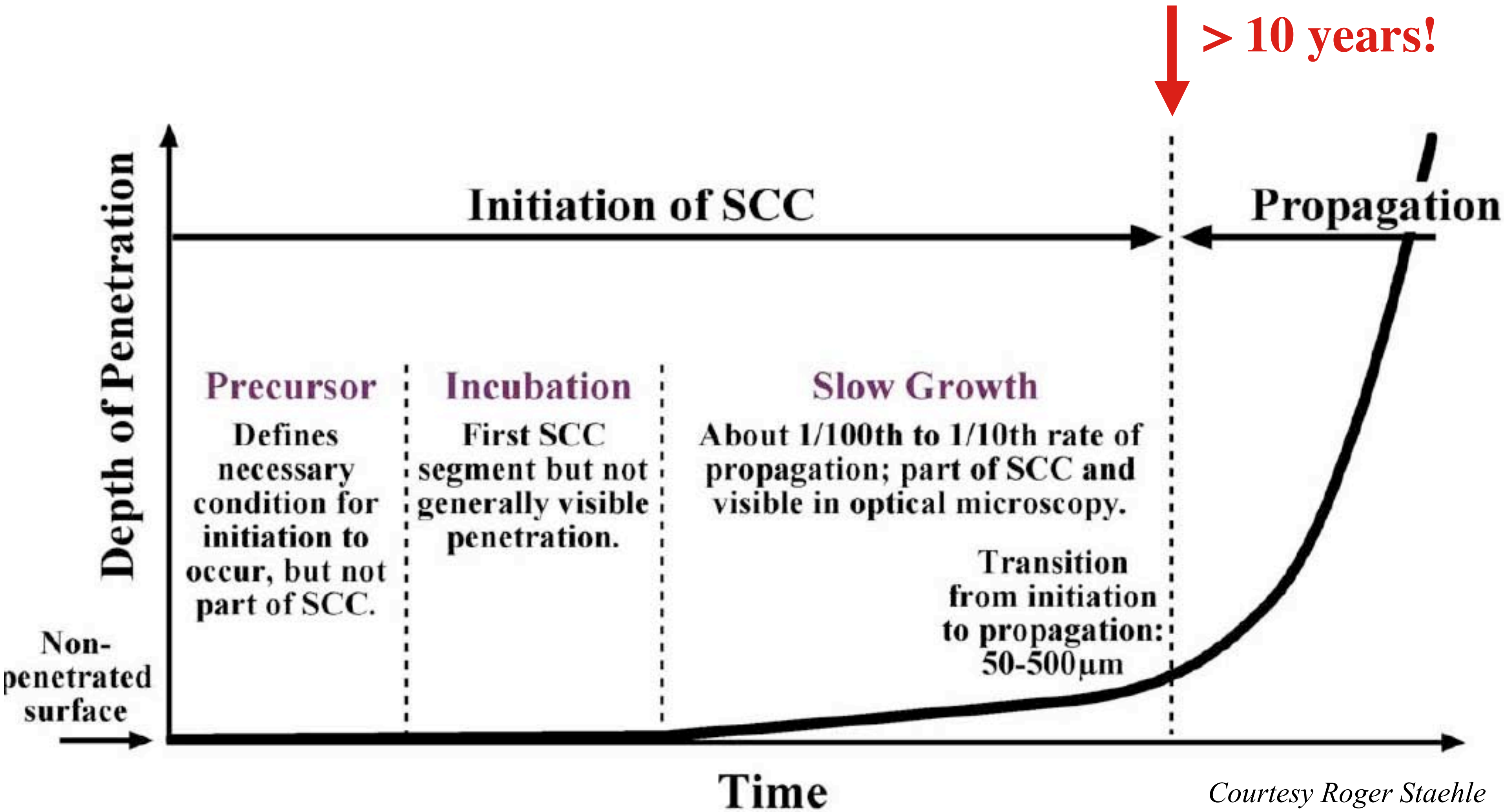
- Ex: Type 316 SS under insulation (after During)
  - Penetration by rinsing water with 60 ppm Cl^-
  - Temperature 50-60 °C
  - SCC in a few months

Longitudinal cracks due to residual stresses



Courtesy Peter Scott

Stages of crack initiation and propagation



Courtesy Roger Staehle

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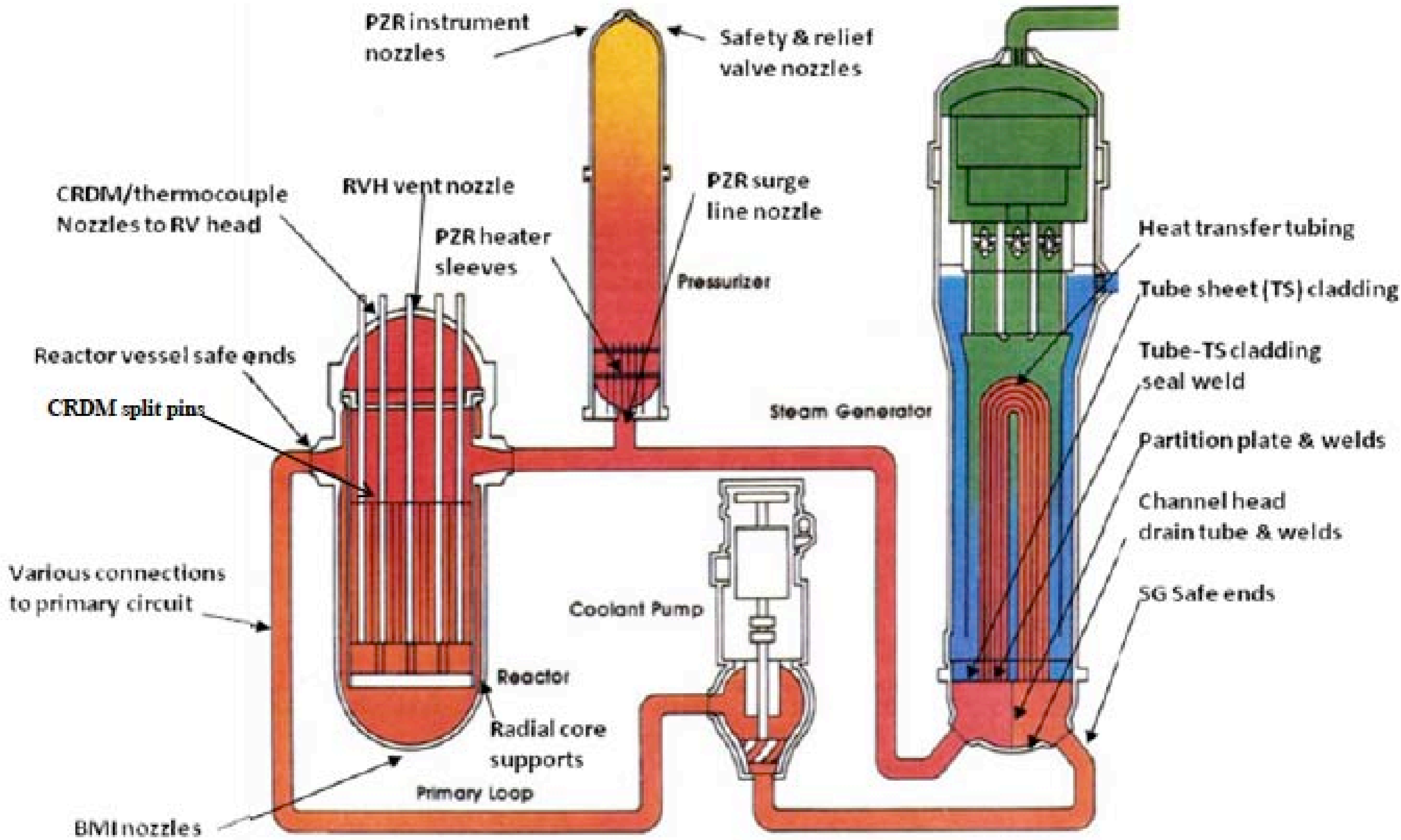
Alloys 600, X-750, 82&182 in PWR Primary Circuit



Courtesy Peter Scott

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SCC of Ni-base Alloys in BWRs

- SCC of Ni-base alloys has been found in several BWRs
  - Cracking of the heat affected zone of Alloy 600 shroud head bolts
  - Cracking of Alloy 182 weld metal in shroud supports and CRD stub tubes.
    - *SCC of shroud support welds is a recent concern for BWRs*
  - Inspection/mitigation necessary - poor accessibility at the bottom of the RPV for repairs.

(after Fujimori 2008)

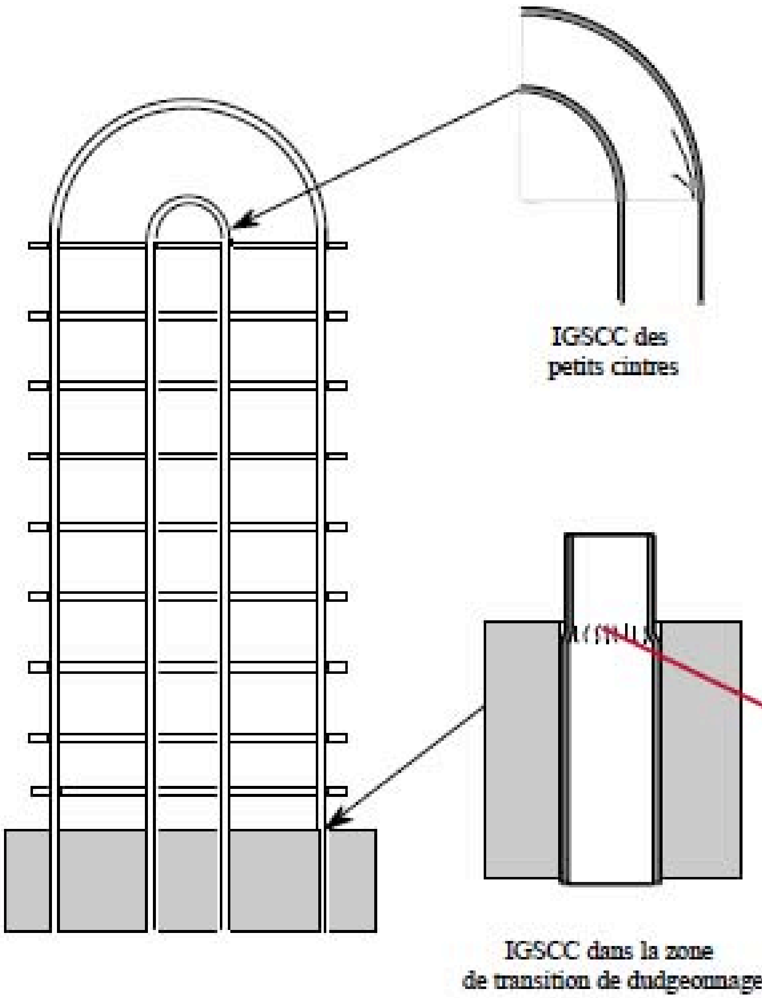
Courtesy Peter Scott

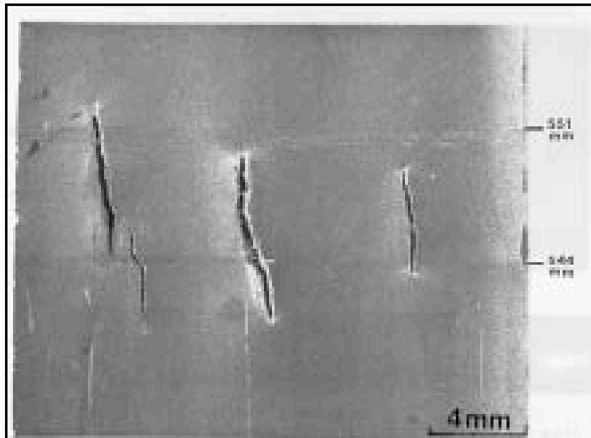
Brief History of Nickel Base Alloys in PWRs

- Cracking in service of Alloy 600 from the 1970s onwards
  - 1980s : Steam generator tubes and Pressurizer sleeves
  - 1990s : Upper Head CRDM nozzles
  - From 2000 : Alloy 182 welds and steam generator divider plates
- Remedies
  - Mid 1970s – Thermal treatment of Alloy 600 for steam generators tubes at ~700°C → Alloy 600 TT - Generally good operating experience
  - Mid 1980s – decision to use Alloy 690 → excellent operating experience - no in-service corrosion induced cracking to date
- From the 1980s to date – management of Alloy 600 in service
  - Development of NDE techniques
  - Empirical models for predicting in-service cracking
- From the early 1990s to date – reliability of Alloy 690TT examined

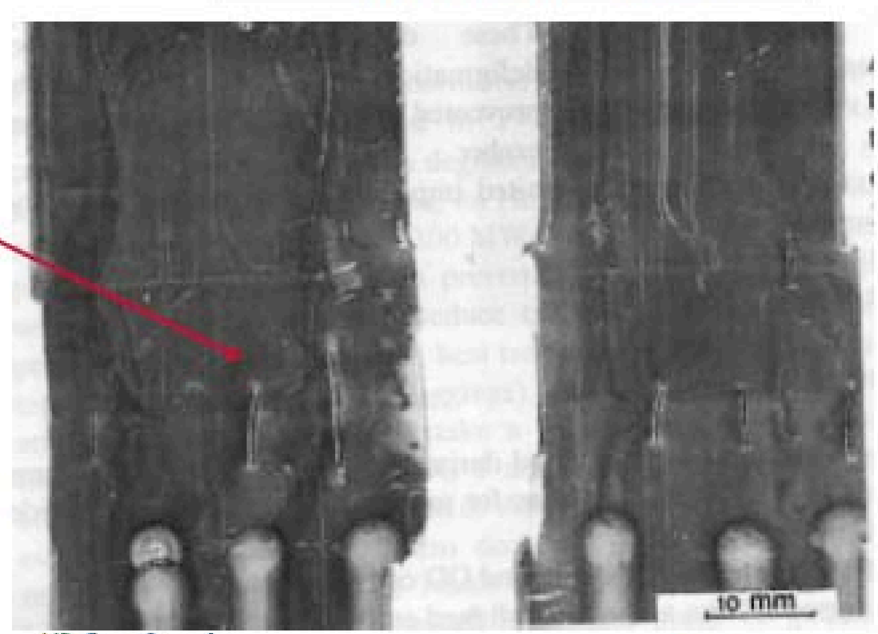
Courtesy Peter Scott

Primary side cracking of Alloy 600 SG tubes





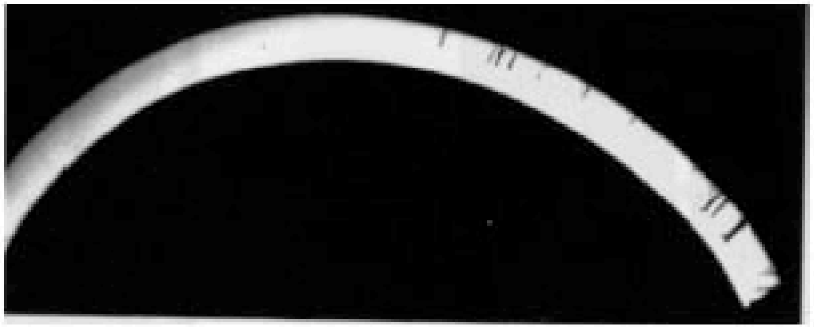
SG tube roll transition from
Bugey 4 (after 62600 h)

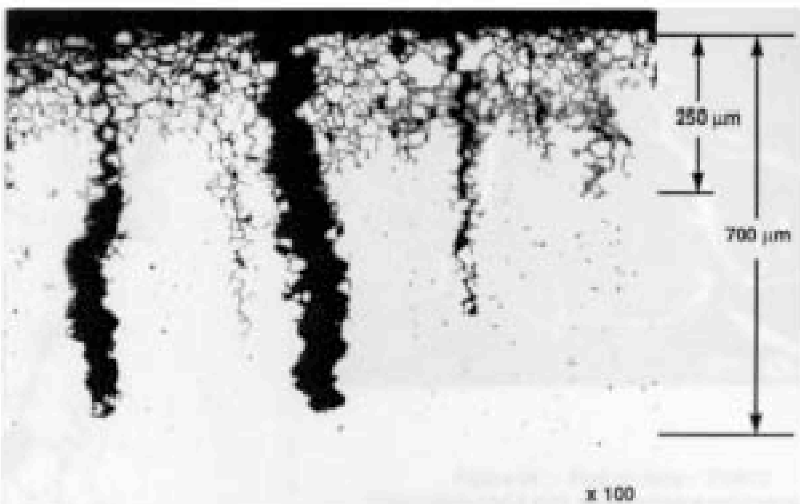


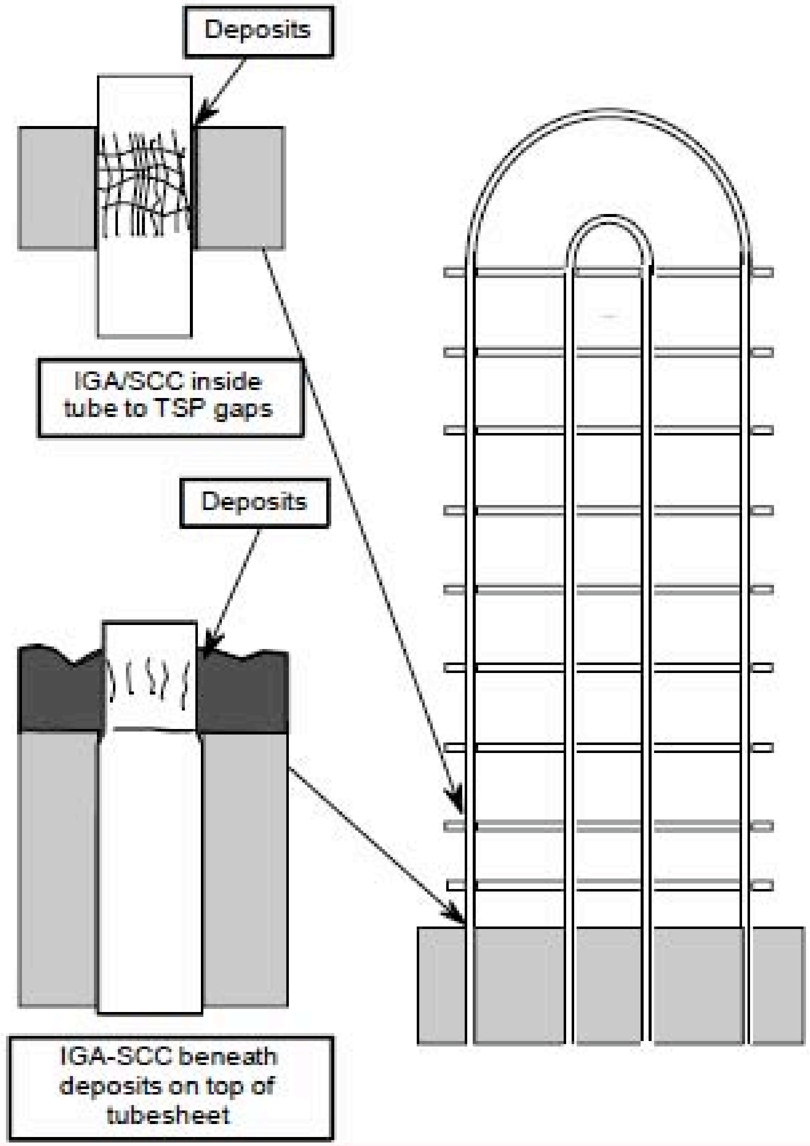
Source: P. Combrade

Secondary side cracking of Alloy 600 SG tubes

- ICA-SCC under deposits formed inside Tube to Tube Support Plate (TSP) gaps or on top of tubesheet

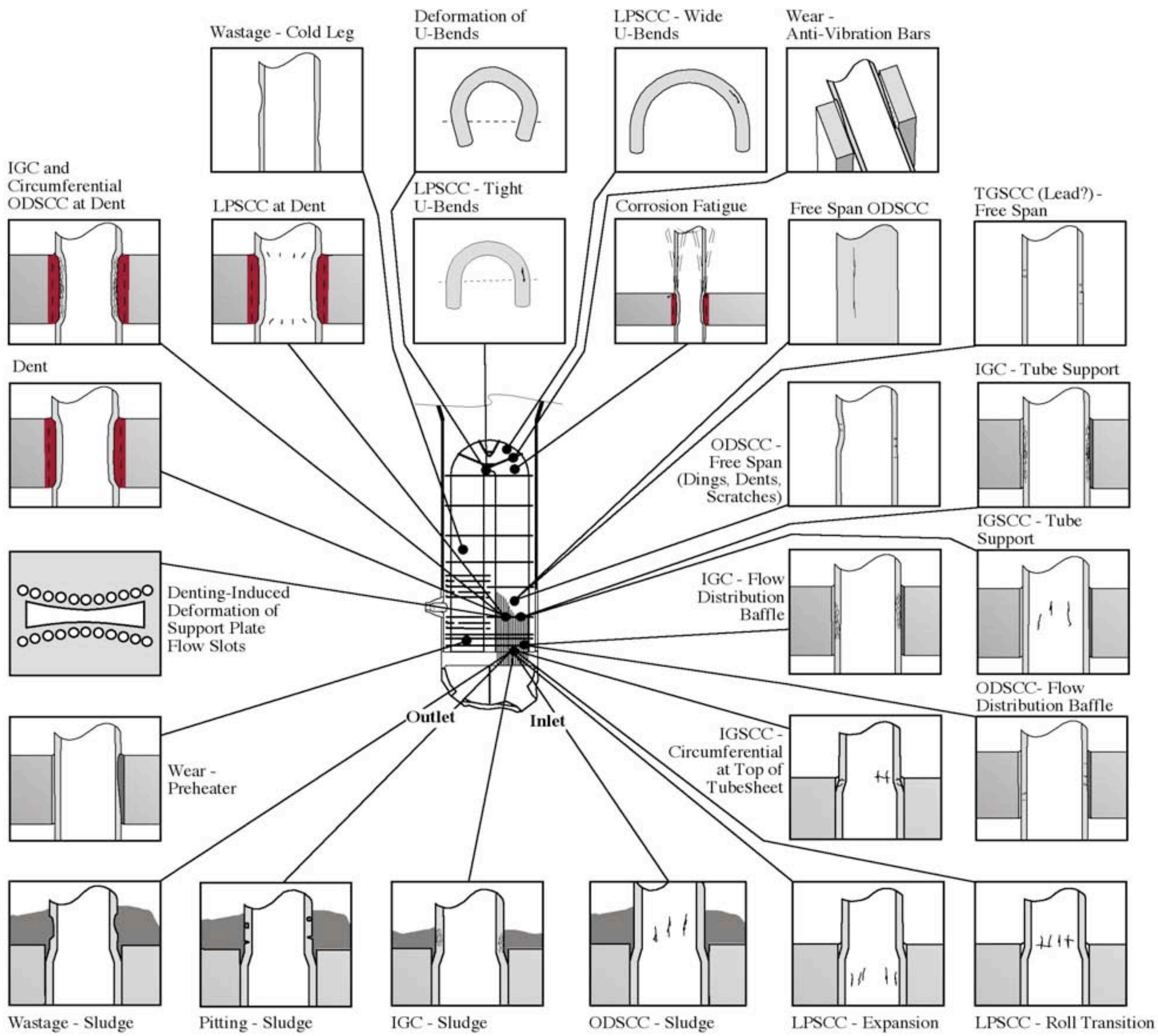






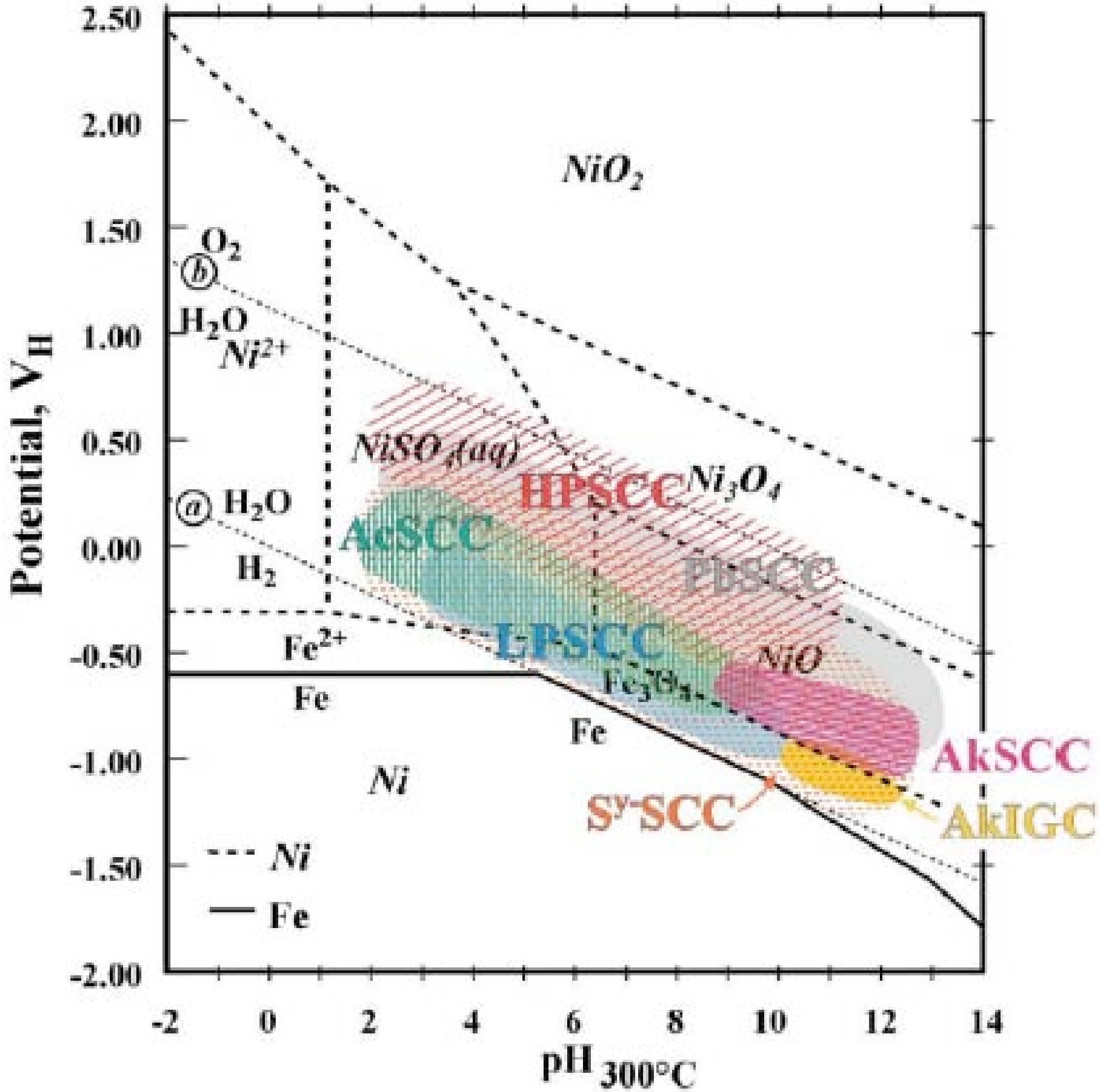
Source: P. Combrade

25 mode-location cases of corrosion with Alloy 600 tubes and drilled hole tube supports



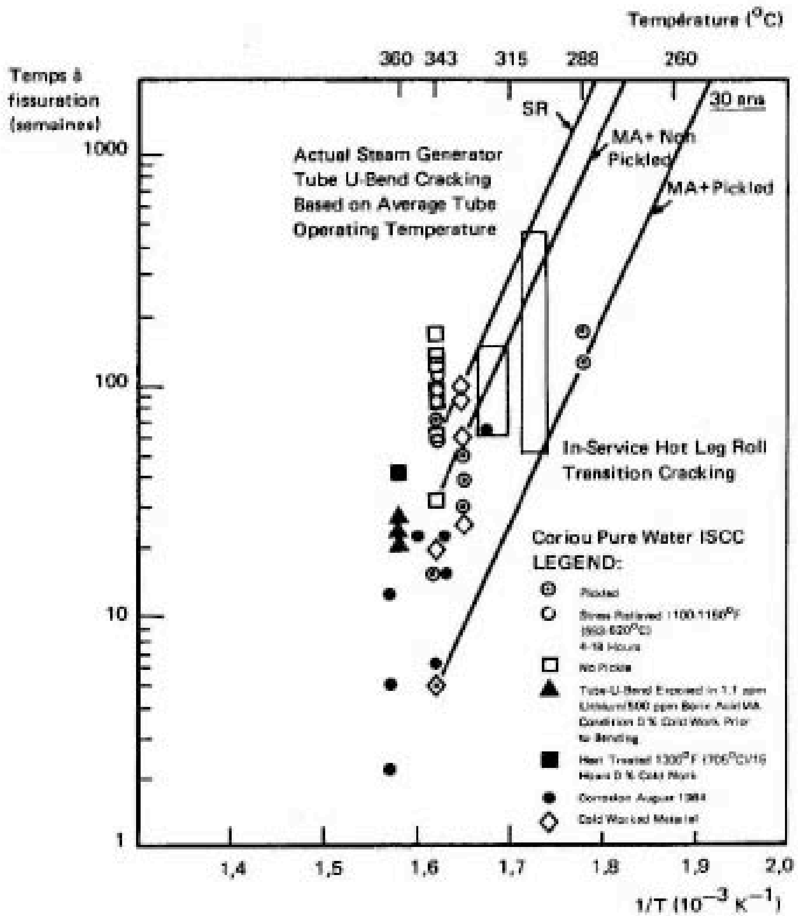
From Staehle and Gorman, 2004

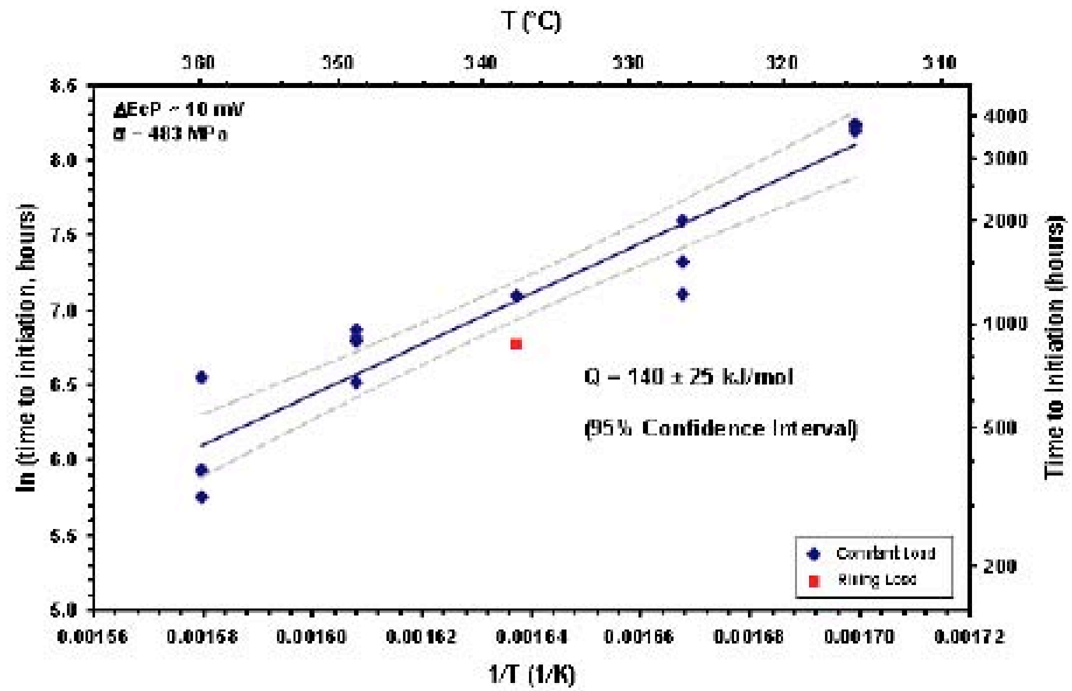
Sub-modes of SCC for Alloy 600 in HT water



Source: R. Staehle

Effect of temperature on crack initiation





Source: P. Combrade

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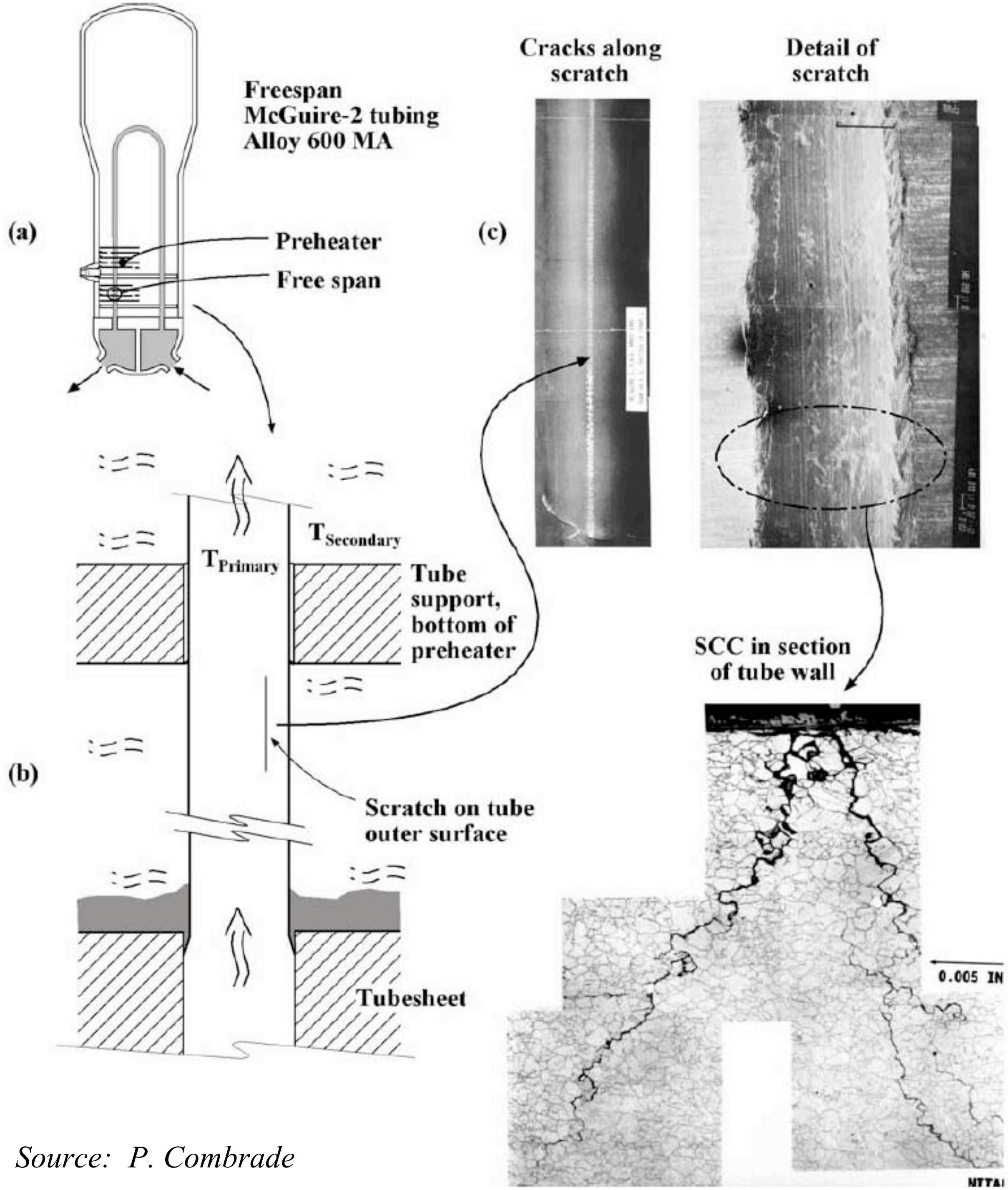
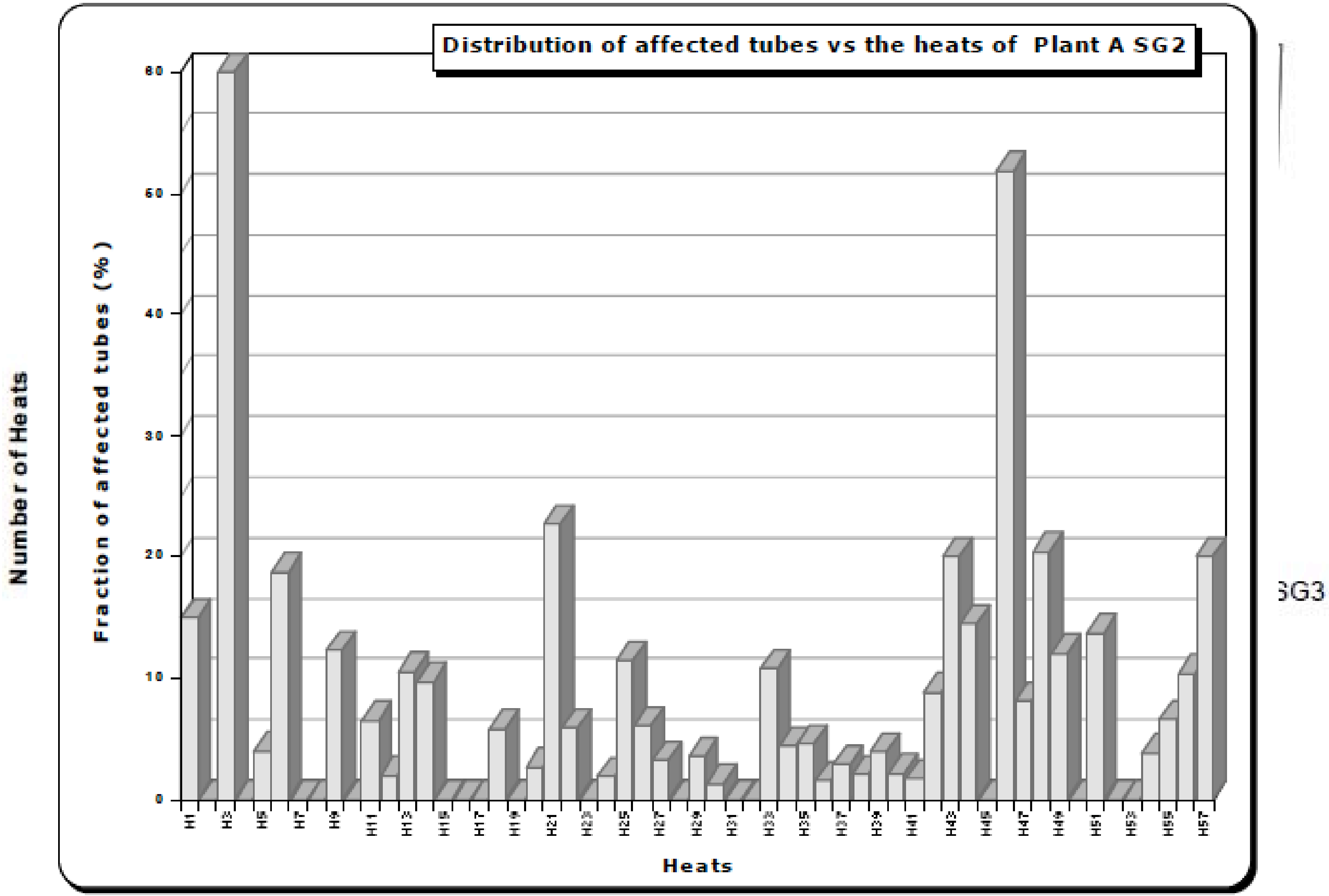
Effect of cold work (scratches)



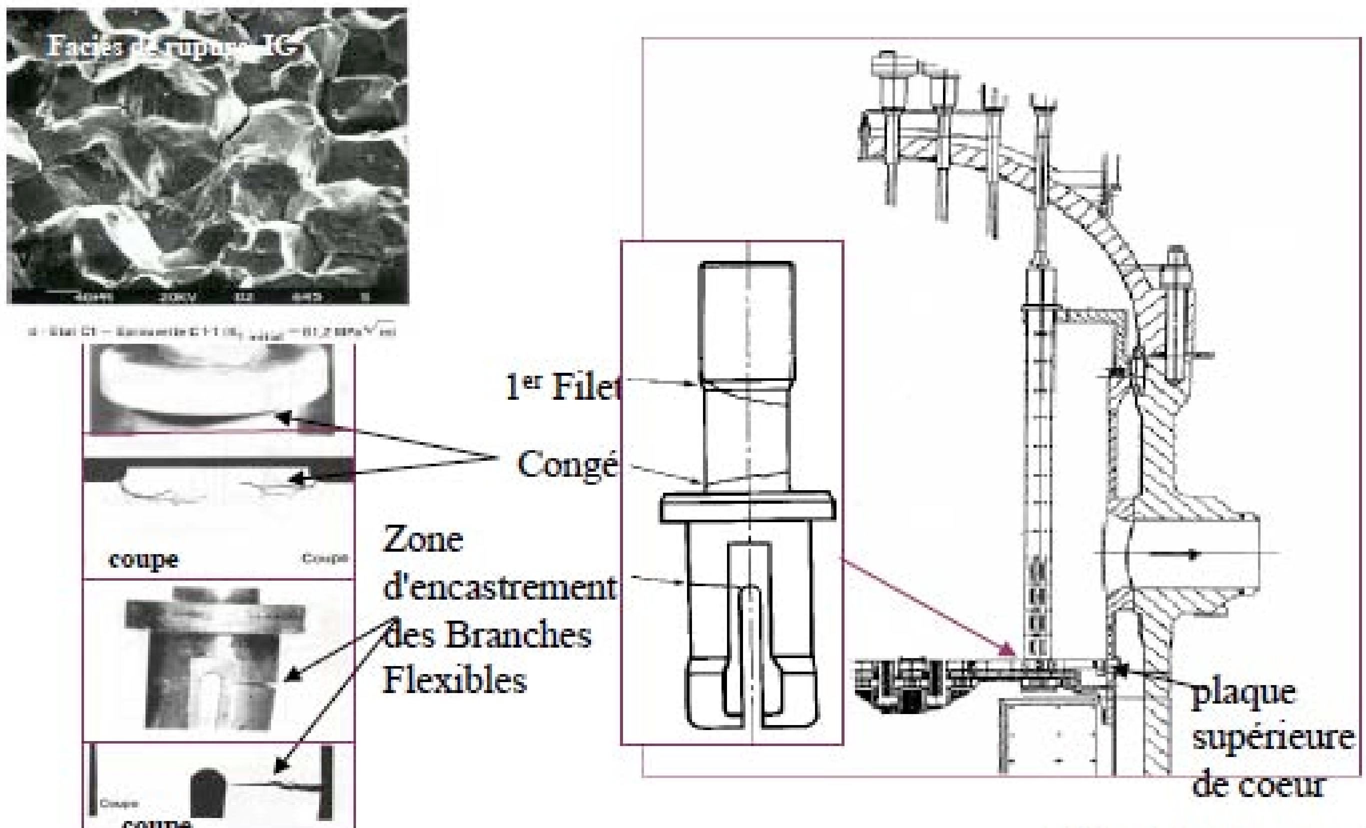
Source: P. Combrade

Metallurgical variables



Source: P. Scott

Alloy X750 Guide Tube Pin Cracking



After Benhamou, 2004

Courtesy Peter Scott

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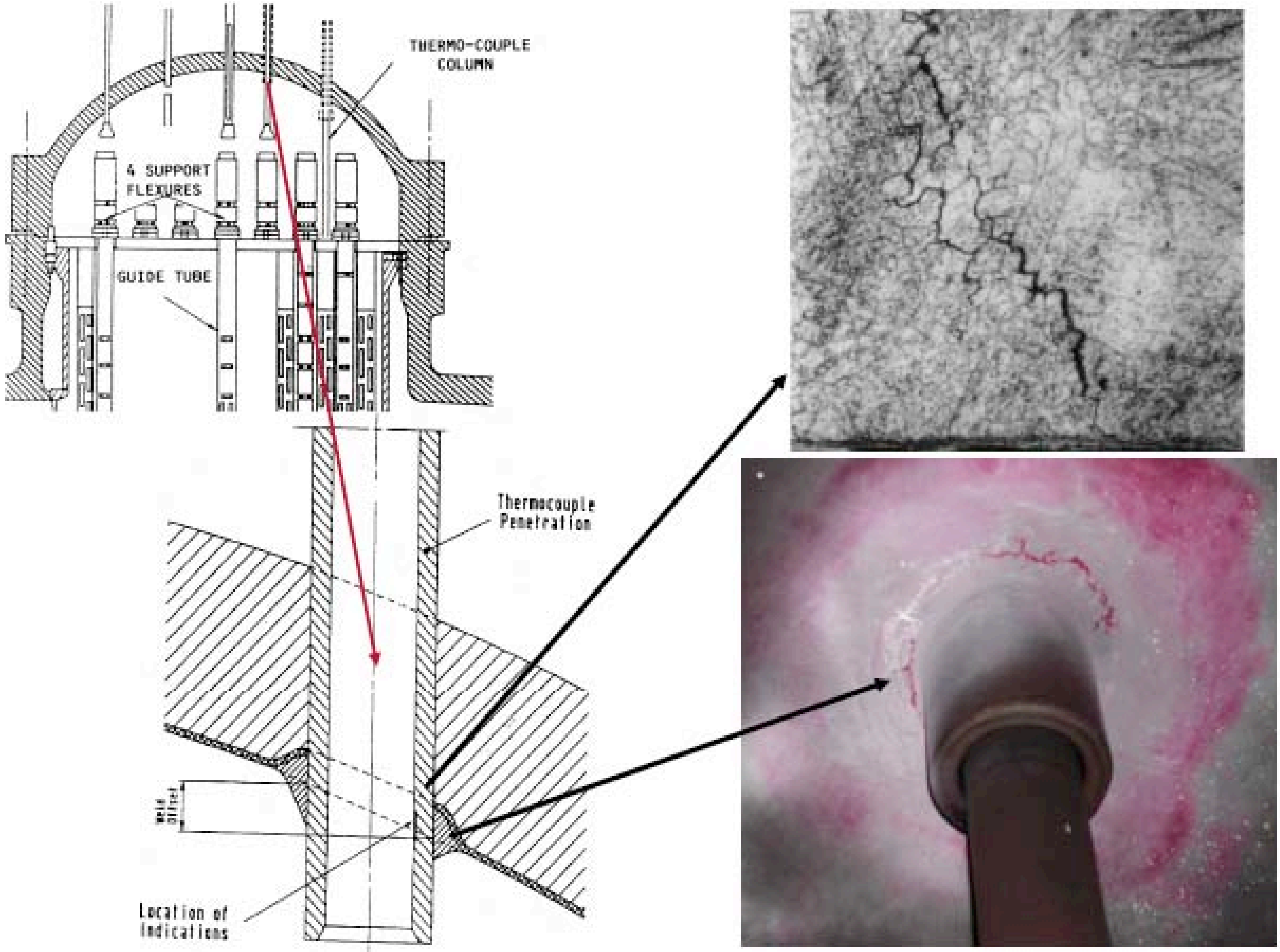
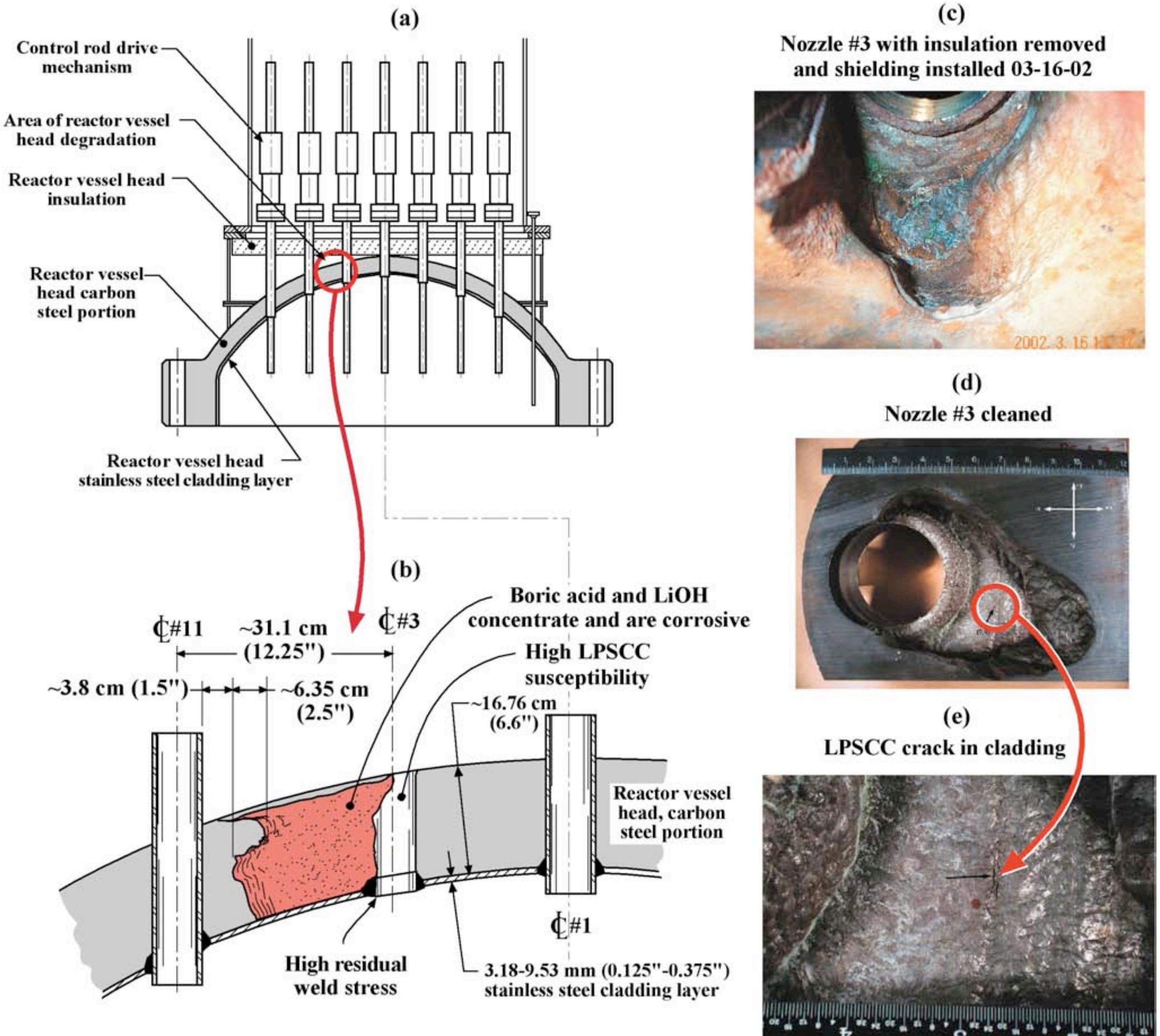
PWSCC in upper head CRDM penetrations



Source: P. Combrade

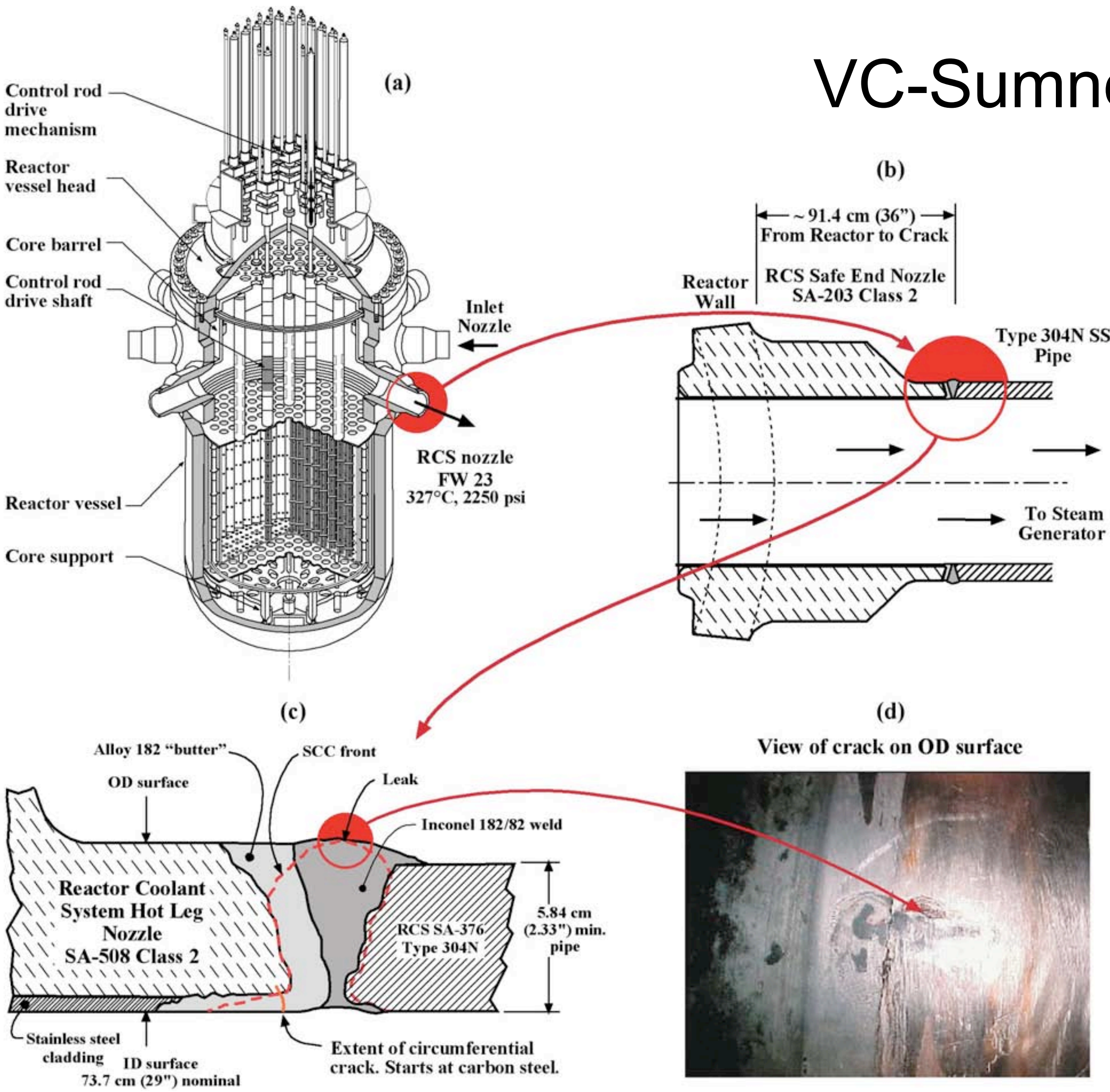
SCC in one component can lead to other forms of corrosion



Source: R. Staehle

SCC has been observed in outlet nozzle weldments

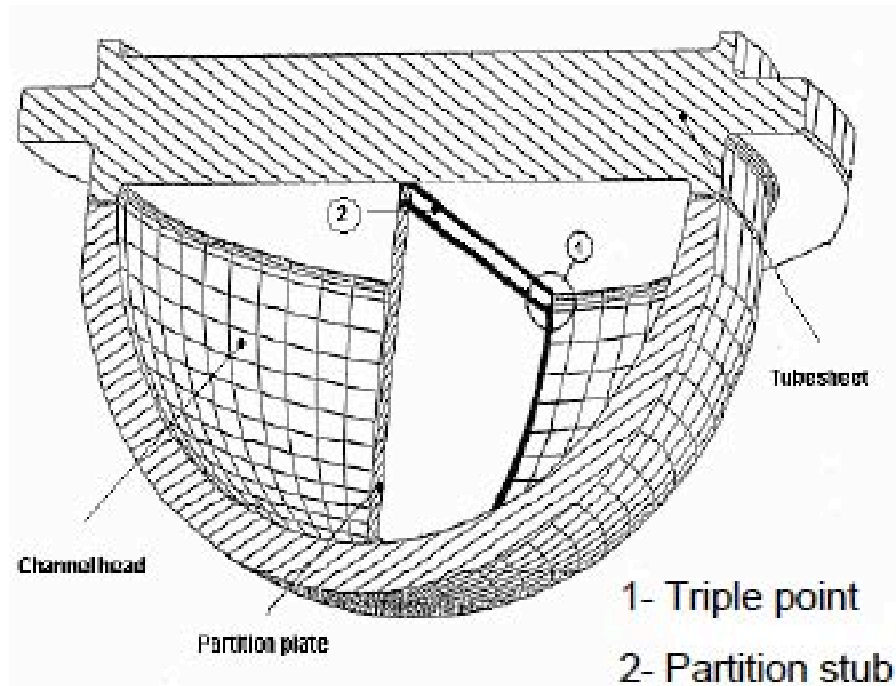
VC-Sumner, 2000

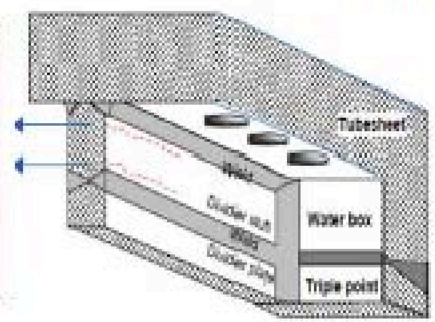


Source: R. Staehle

Steam Generator Channel Head

- SG divider plates
  - 12 SG affected out of 87 inspected
  - Cracks on the hot-leg side of the stub runner
  - Mainly located in two lines parallel to the weld axis
  - No cracks in the divider plate itself
  - Superficial cracks - depth < 2 mm in most cases
  - No propagation after successive inspections

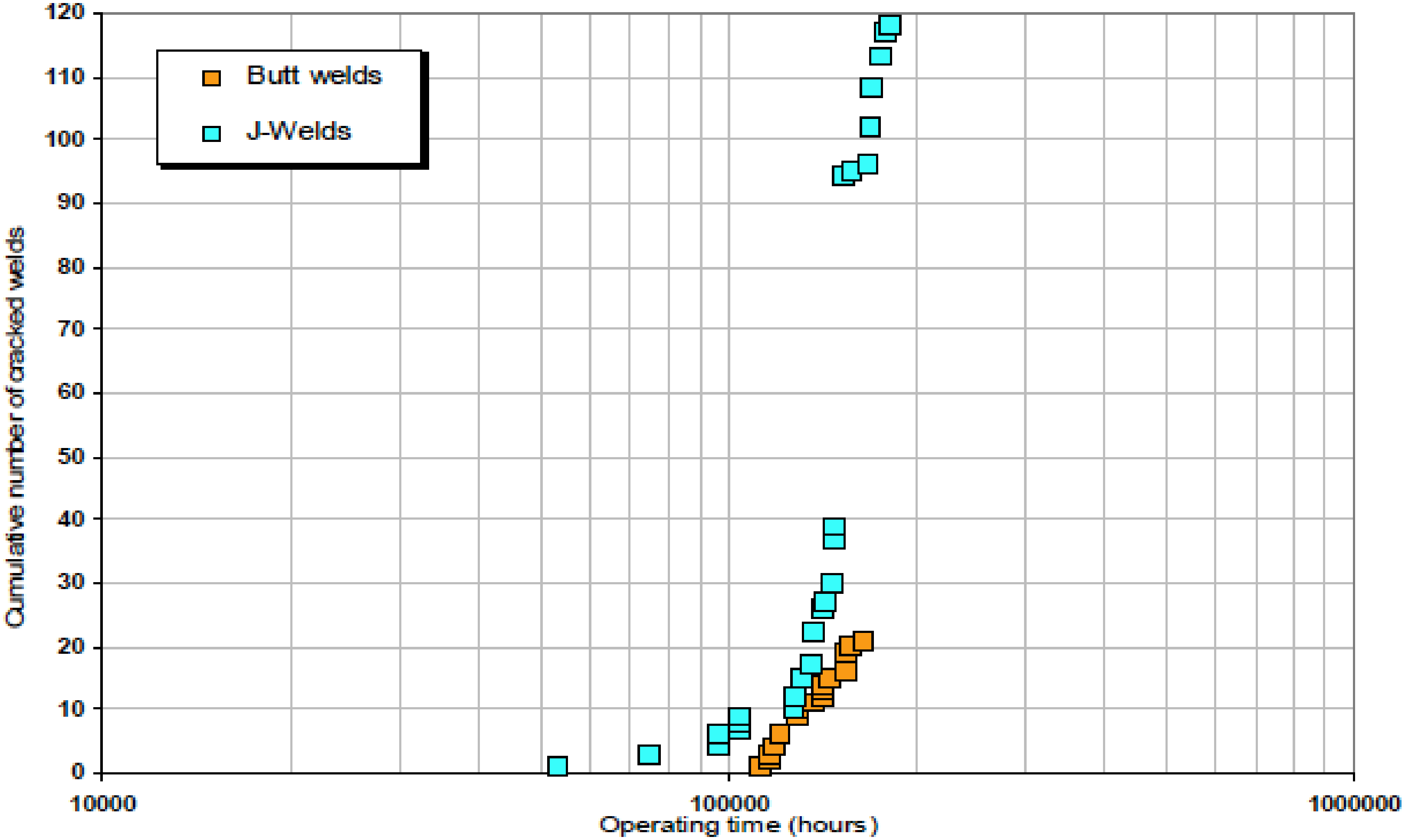




After Déforge et al, 2010

Courtesy Peter Scott

Operating times to Alloy 182 Weld Cracking
(for different types of welds)



Courtesy Peter Scott

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Incidence of Stress Corrosion Cracking in Nickel-Base Alloys in PWRs

- Only cold worked and/or as-welded Alloy 600/182/82 components have been affected so far
- Components subjected to heat treatment due to stress relief of adjacent low alloy steel components (typically 610°C for 10 hours) have not cracked to date:
  - Mockup studies show that the surface residual stress is very significantly reduced even though the stress relief temperature is not optimized for nickel base alloys
  - Microscopic examination shows that stress relief occurs due to recrystallization during heat treatment of heavily cold worked surface layers from grinding

Courtesy Peter Scott

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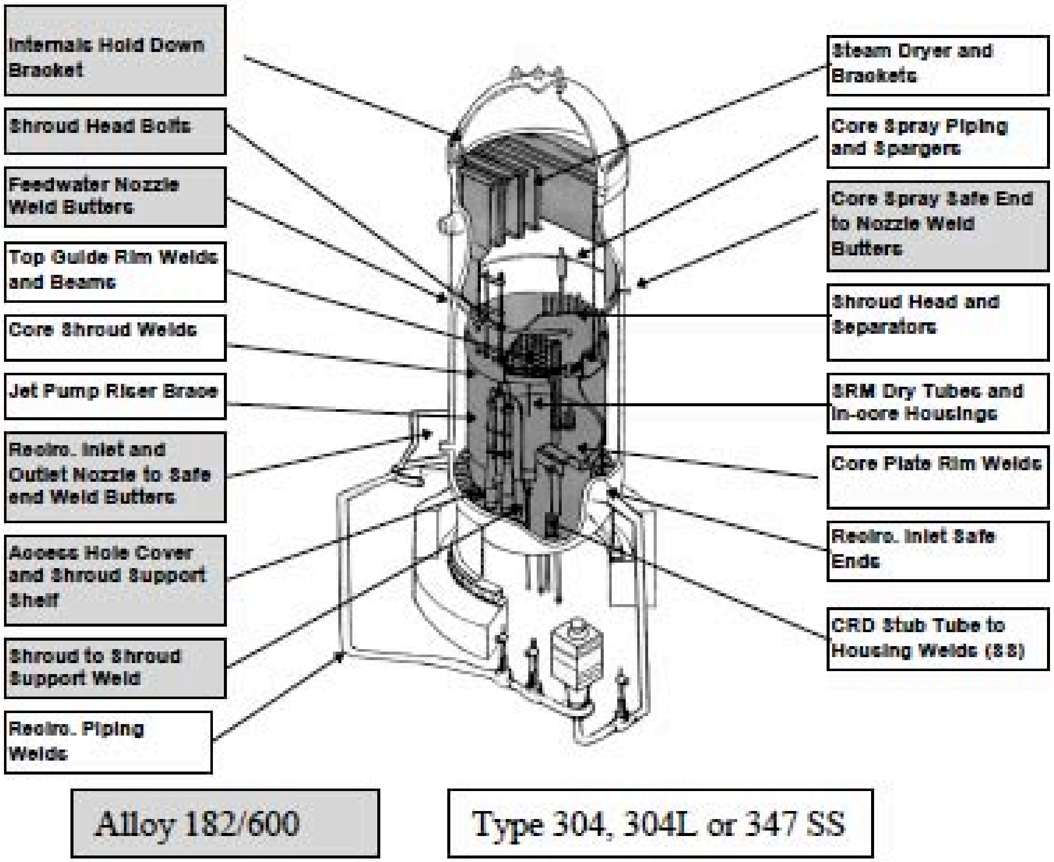
Field Experience of SCC in Austenitic Stainless Steels in PWRs

- Austenitic stainless steels Type 304 or 316 have generally performed very well in PWR primary water service with relatively few service failures associated with the following
  - Very high levels of cold work
  - Presence of solution impurities in dead legs, e.g. Cl^- , SO_4^- and O_2
  - High neutron doses
- Failures for SA 453 Grade 660 (A 286) bolting due to stress corrosion cracking in primary water have been reported due to excess preload or bad design (shank to head radius)

Courtesy Peter Scott

BWR SS Piping --> Core Components



(From Andresen, 2008)

Stress Corrosion Cracking History:

1969 1st detected in sensitized SS

1970s Stainless steel welded piping

1980s BWR internals

1990s Low stress BWR internals, CW & crevices

2000s Internals, CW

Courtesy Peter Scott

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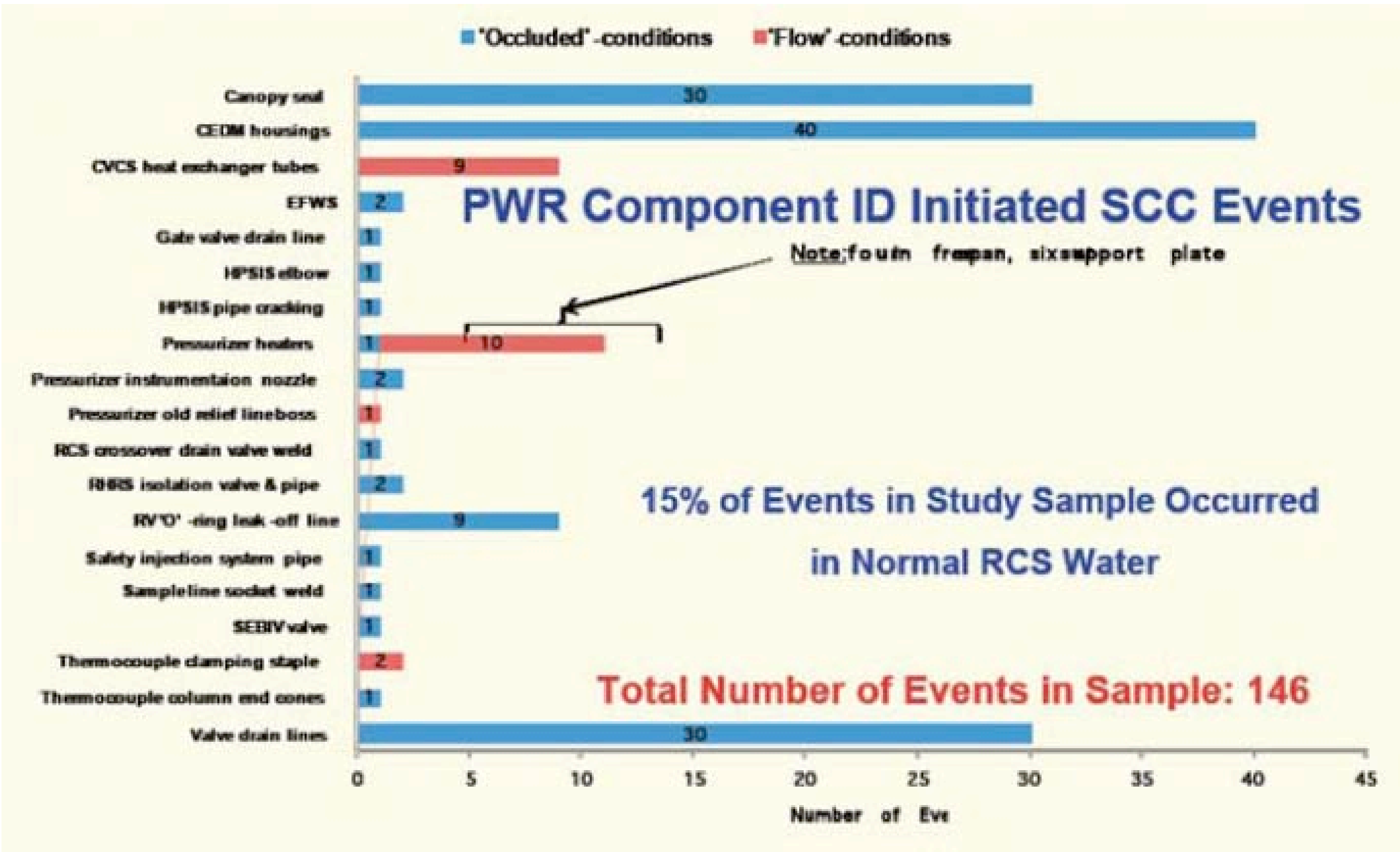
Summary of SCC of Austenitic SSs in PWR Primary Circuits



Ilevbare et al. 2007-09

There is a clear association between the incidence of cracking and hardness>300 HV but plant age is not A risk factor. Thermal sensitization is only important in occluded zones. The phenomenon in "normal RCS water" is often (unfortunately) labeled "PWSCC".

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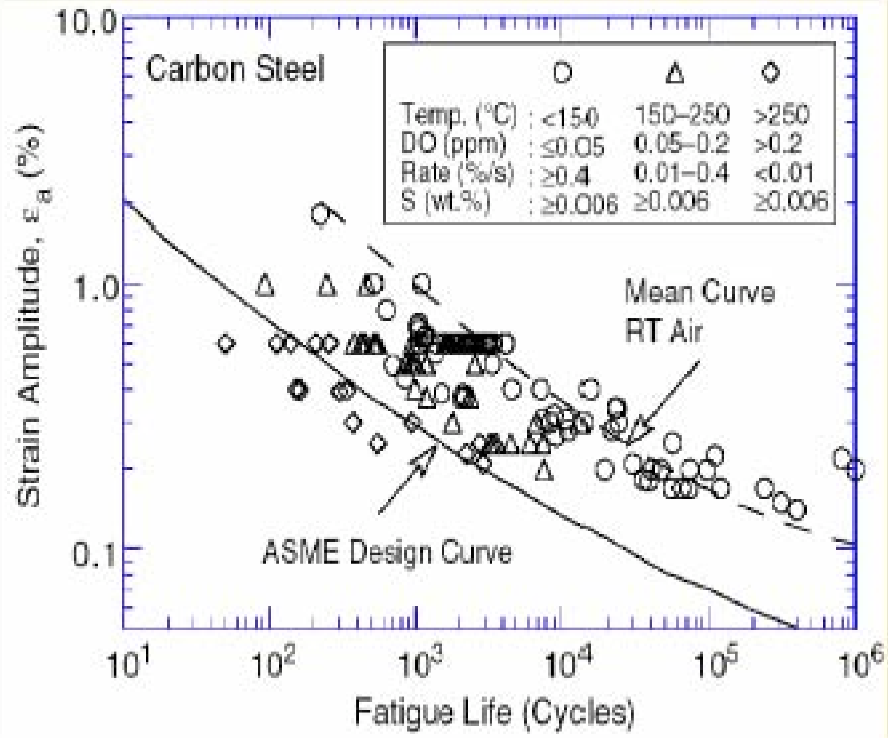
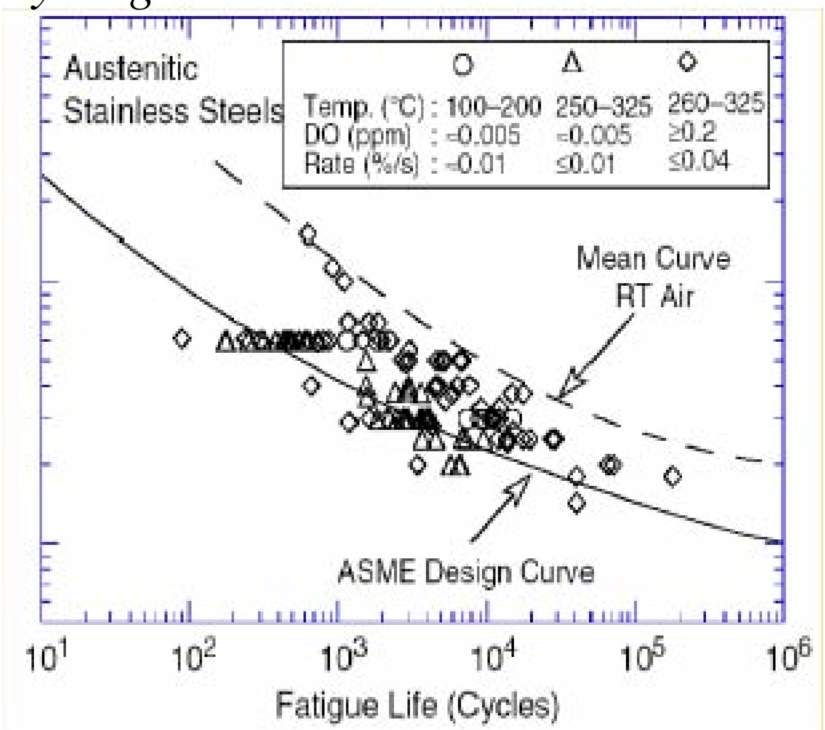
Fatigue and Corrosion Fatigue

Degradation of fatigue strength of low carbon & LAS steels at high potential is caused by dissolution of MnS inclusions.



Degradation of fatigue strength of low stainless steel at low potential could be due to their higher corrosion rate compared to high potential or due to hydrogen.



Courtesy Peter Scott

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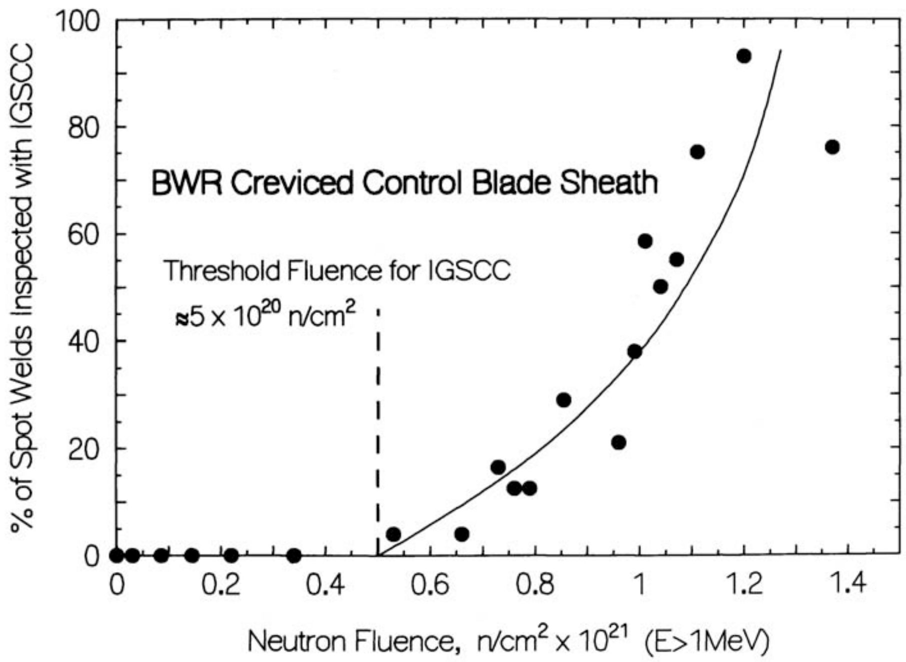
IASCC service experience

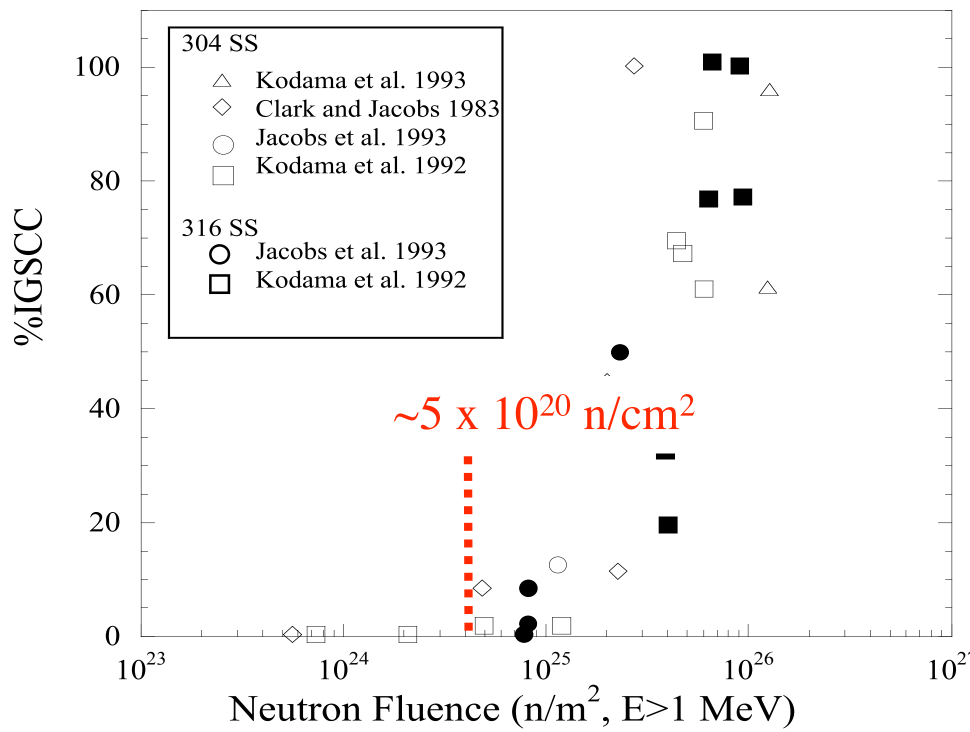
Component	Material	Reactor Type	Possible Sources of Stress
Fuel Cladding	304 SS	BWR	Fuel Swelling
Fuel Cladding	304 SS	PWR	Fuel Swelling
Fuel Cladding *	20%Cr/25%Ni/Nb	AGR	Fuel Swelling
Fuel Cladding Ferrules	20%Cr/25%Ni/Nb	SGHWR	Fabrication
Neutron Source Holders	304 SS	BWR	Welding & Be Swelling
Instrument Dry Tubes	304 SS	BWR	Fabrication
Control Rod Absorber Tubes	304/304L/316L SS	BWR	B_4C swelling
Fuel Bundle Cap Screws	304 SS	BWR	Fabrication
Control Rod Follower Rivets	304 SS	BWR	Fabrication
Control Blade Handle	304 SS	BWR	Low stress
Control Blade Sheath	304 SS	BWR	Low stress
Control Blades	304 SS	PWR	Low stress
Plate Type Control Blade	304 SS	BWR	Low stress
Various Bolts **	A-286	PWR & BWR	Service
Steam Separator Dryer Bolts **	A-286	BWR	Service
Shroud Head Bolts **	600	BWR	Service
Various Bolts	X-750	BWR & PWR	Service
Guide Tube Support Pins	X-750	PWR	Service
Jet Pump Beams	X-750	BWR	Service
Various Springs	X-750	BWR & PWR	Service
Various Springs	718	PWR	Service
Baffle Former Bolts	316 SS Cold Work	PWR	Torque, differential swelling
Core Shroud	304/316/347 /L SS	BWR	Weld residual stress
Top Guide	304 SS	BWR	Low stress (bending)

IASCC has been realized both in-plant and in laboratory experiments

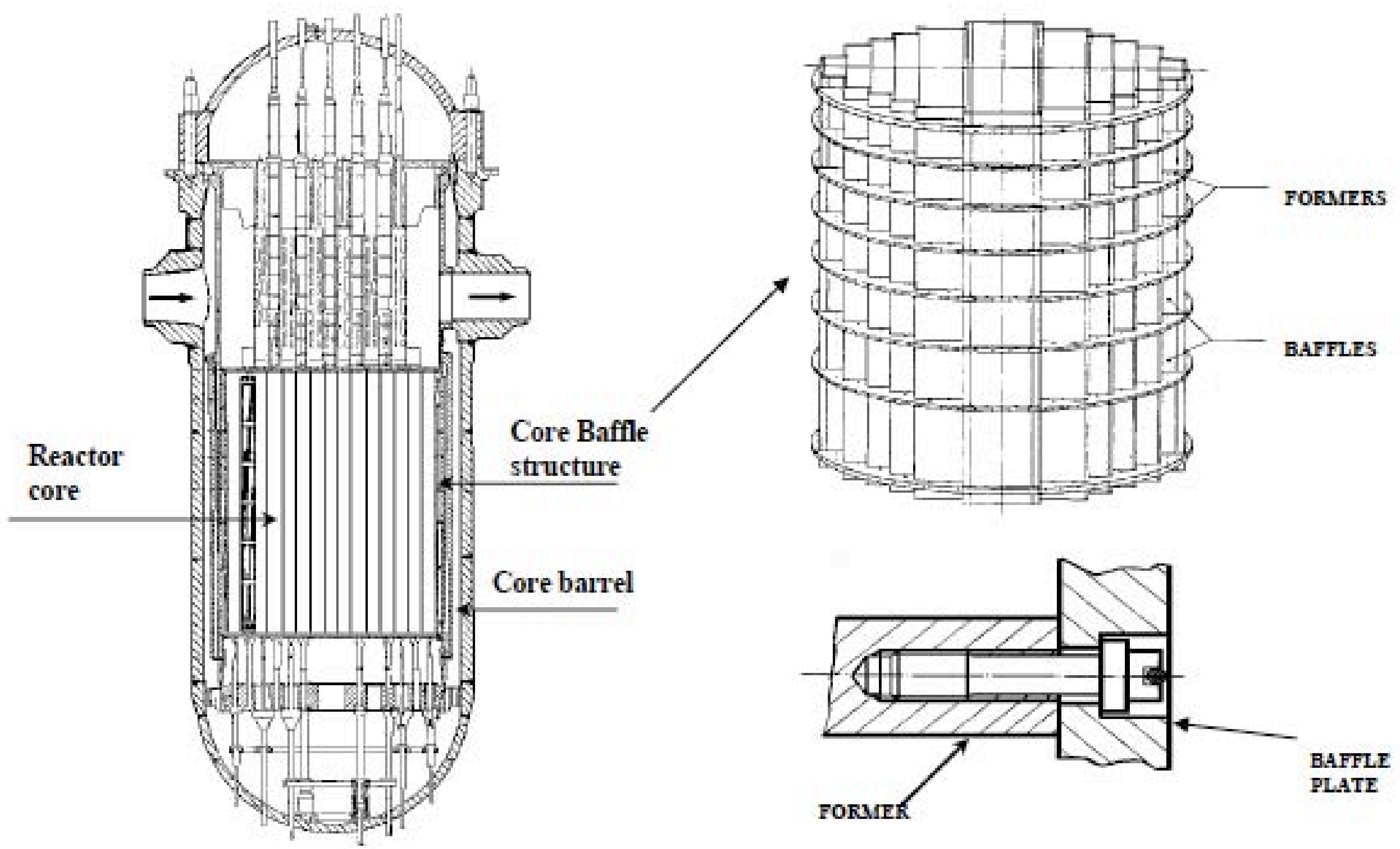
Plant



Laboratory



Pressure Vessel and Core Components of a PWR-Baffle-Formaer Bolt Cracking



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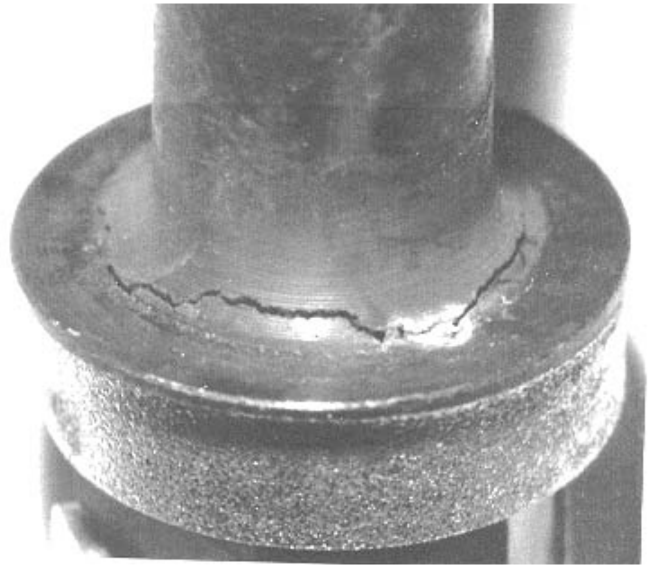
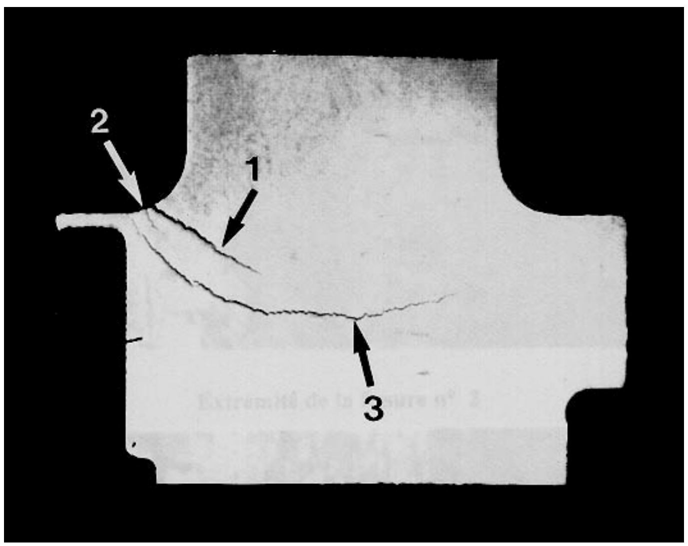
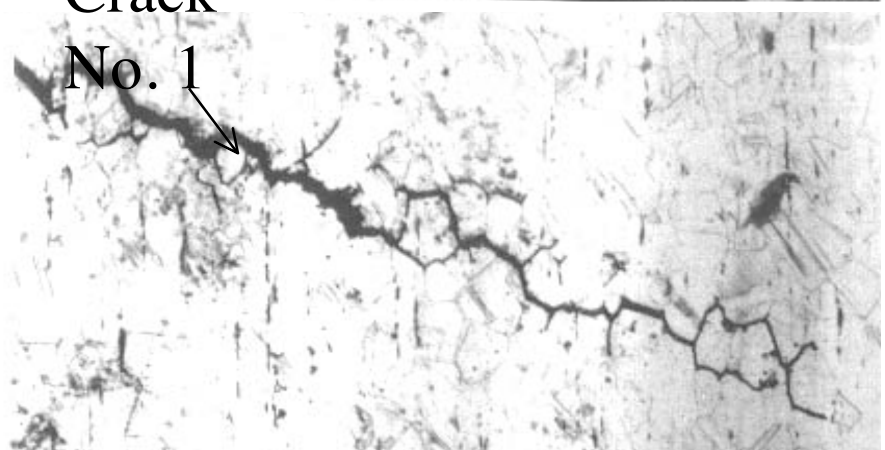
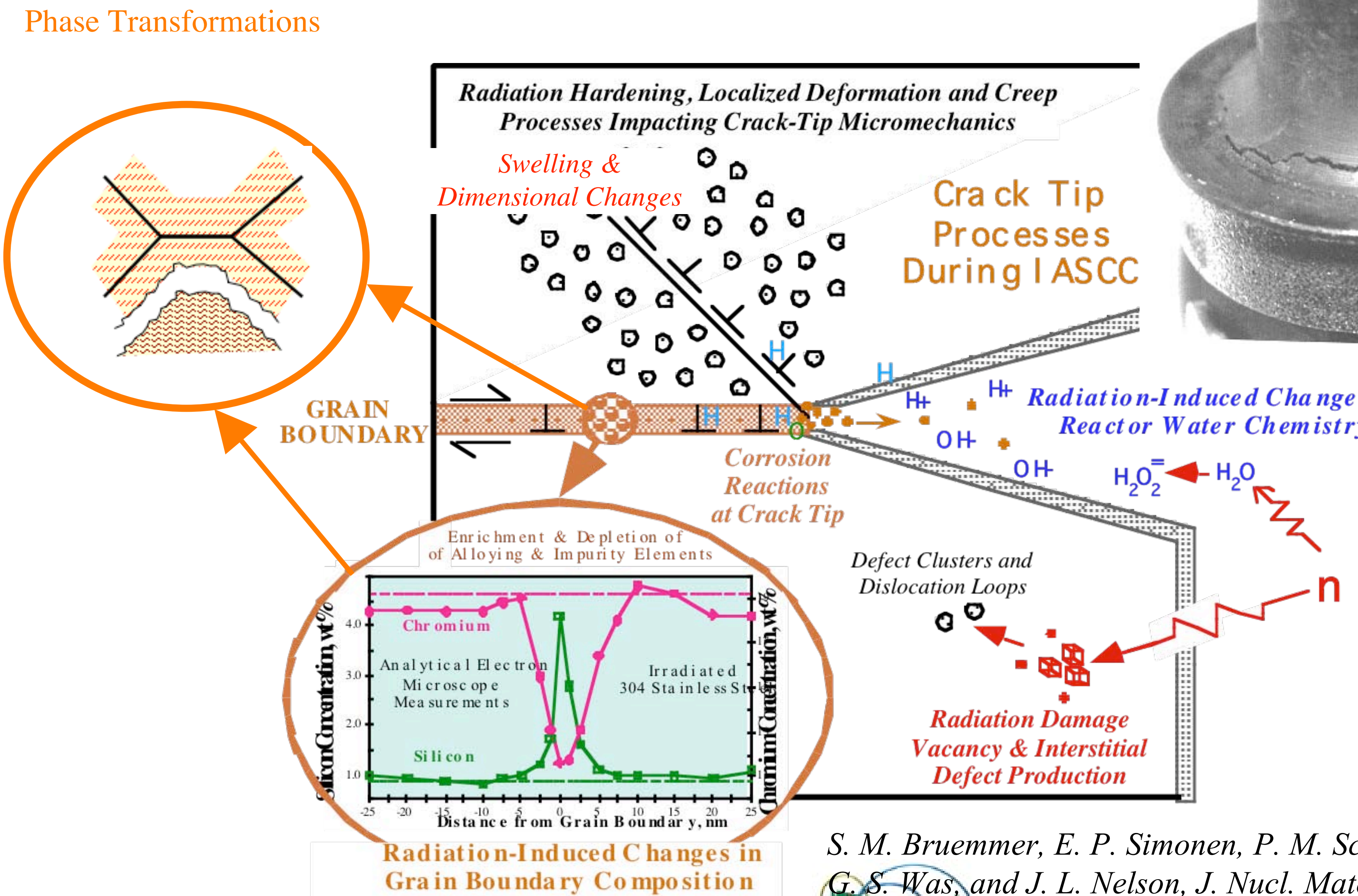
Baffle bolts experience some of the highest fluences and temperatures in a PWR core

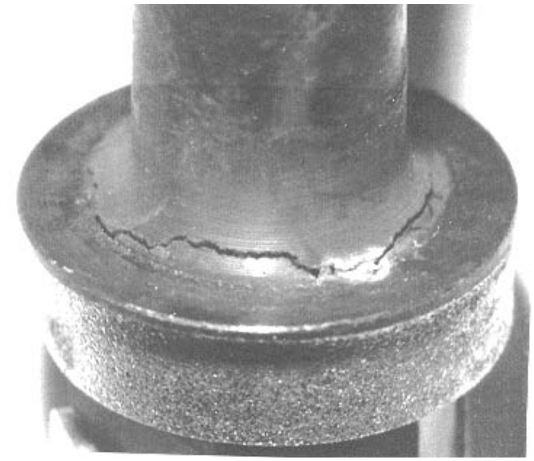






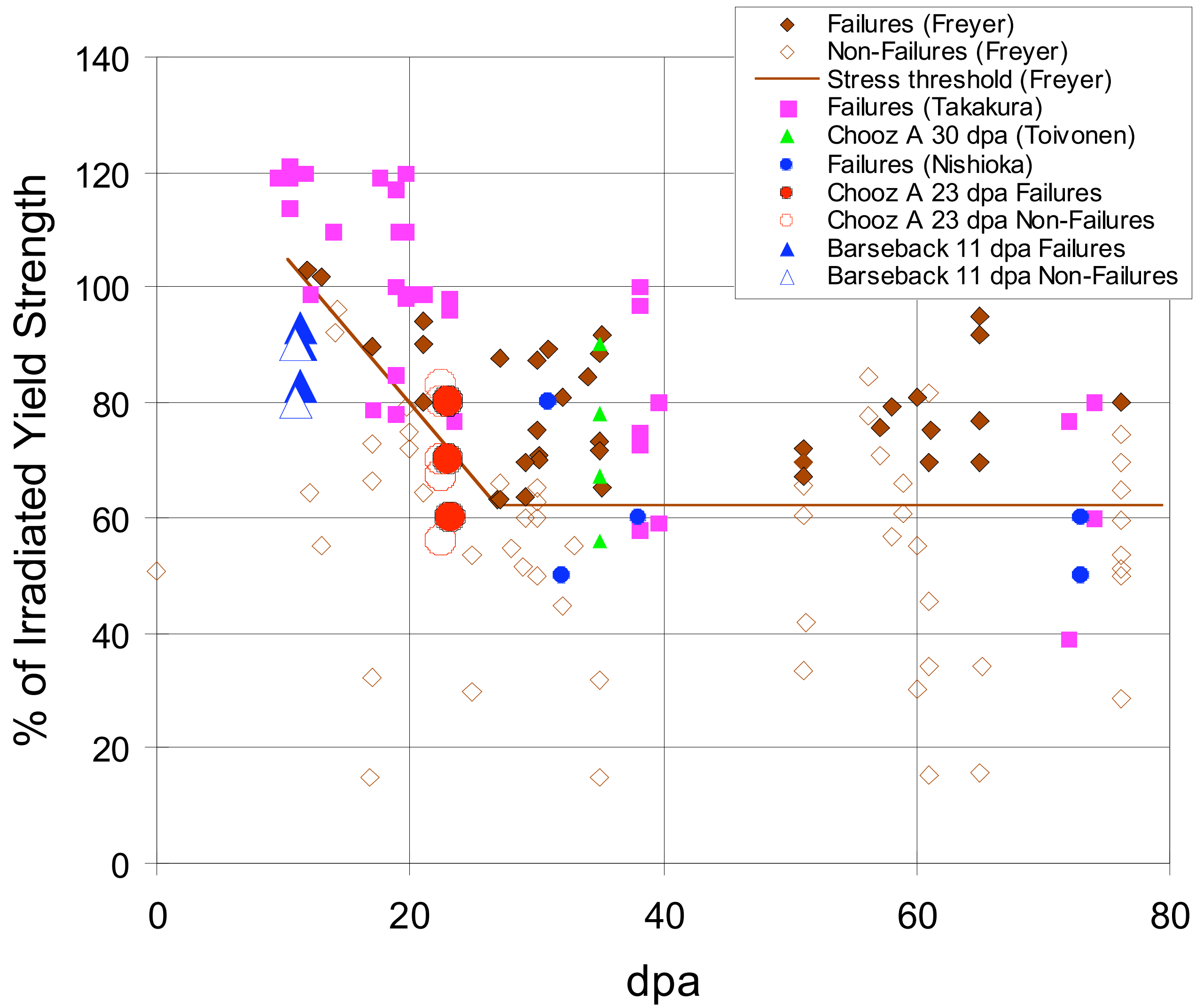
Many different irradiation processes influence material performance as well as susceptibility to cracking





S. M. Bruemmer, E. P. Simonen, P. M. Scott, P. L. Andresen, G. S. Was, and J. L. Nelson, J. Nucl. Mater., 274 (1999)p 299.

Failure as a percent of irradiated yield strength vs. dose



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CIR final report, 2010

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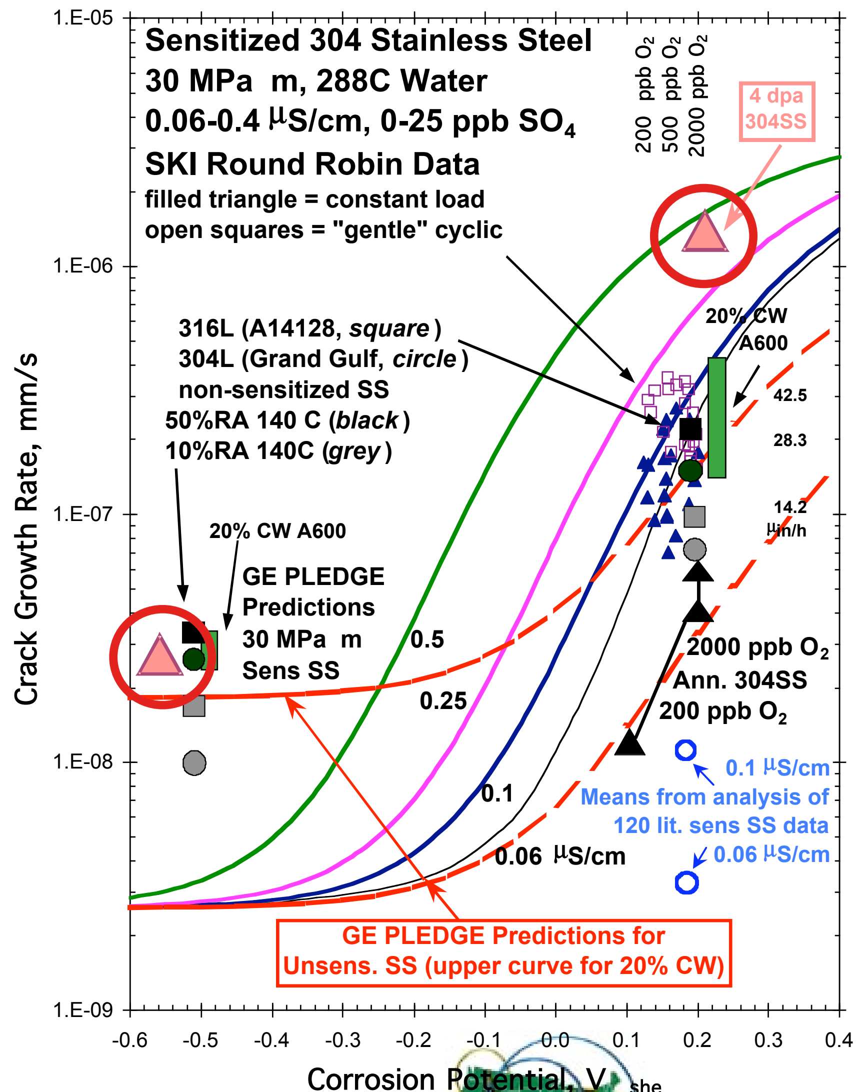
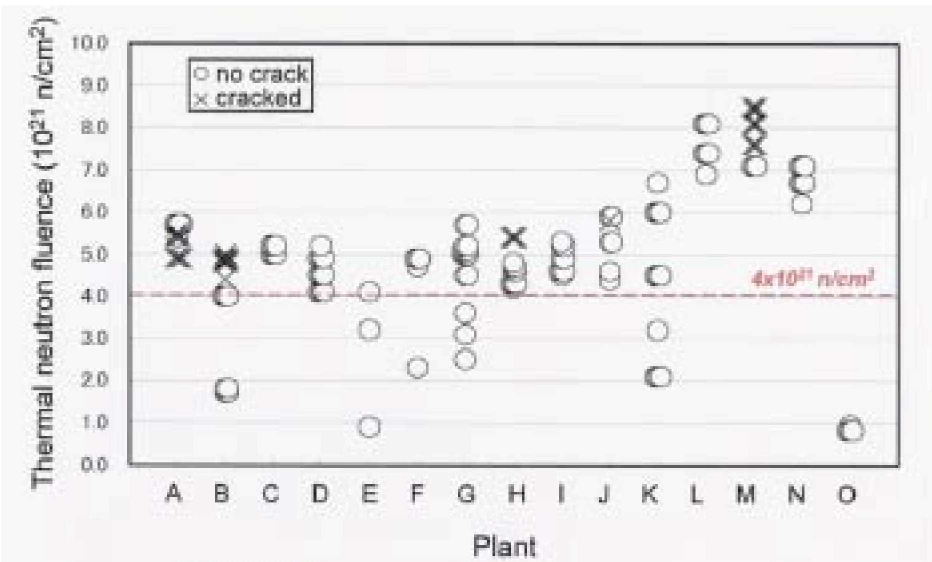
Effect of irradiation on crack growth in stainless steels in high temperature water



Was, Busby and Andresen, ASM Handbook, Vol. 13c 2006.

Summary of IASCC in BWRs

- SCC of 316L(NG)/304L core shrouds and has been found in many BWRs
  - *Elimination of surface cold work is important during fabrication*
  - *Neutron and gamma-ray irradiation may assist cracking*
- IASCC of 316L has been found in handles and sheaths in many control rods
  - *Crevices should be avoided in the core region*



Neutron fluence dependence of control rod sheath cracking

After Fujimori 2008

General corrosion is the dominant form of degradation of fuel cladding

- In primary environment (water or steam), Zr alloy cladding undergoes corrosion according to following chemical reaction

$$Zr + 2H_2O \rightarrow ZrO_2 + 2(1 - w)H_2(\text{coolant}) + 4w\ H(\text{metal})$$

w : fraction of reaction produced hydrogen absorbed by the metal

- Progressive formation of a ZrO_2 layer
- Hydriding of the cladding metal bulk

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Source: B. Cheng

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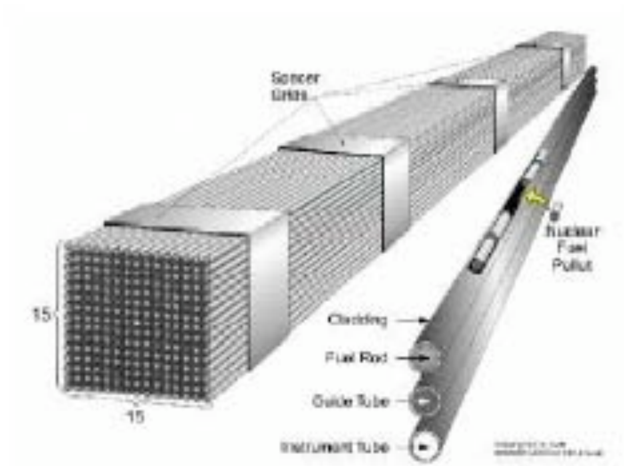
General corrosion is the dominant form of degradation of fuel cladding

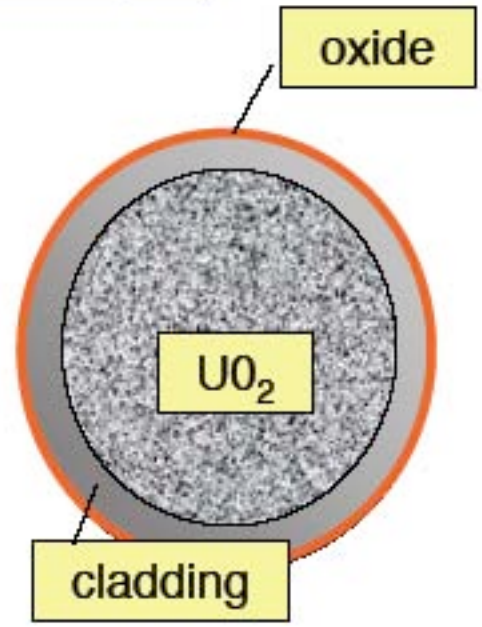
- In a primary environment, Zr alloys undergo corrosion

Oxidation

Hydrogen Pickup

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$$





- Progressive growth of a ZrO_2 layer
- Hydrogen uptake results in hydriding of the cladding

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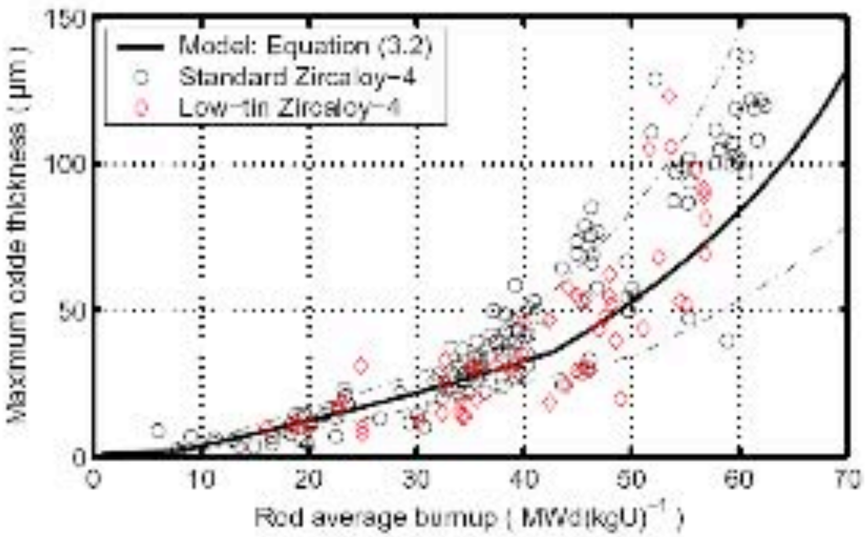
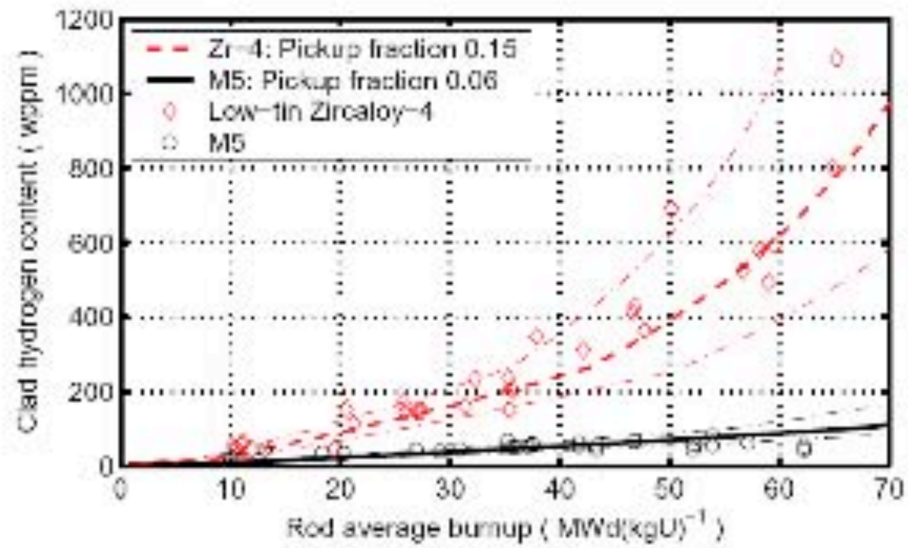
Hydrogen content correlates with oxide thickness

oxide thickness



hydrogen content



Source: B. Cheng

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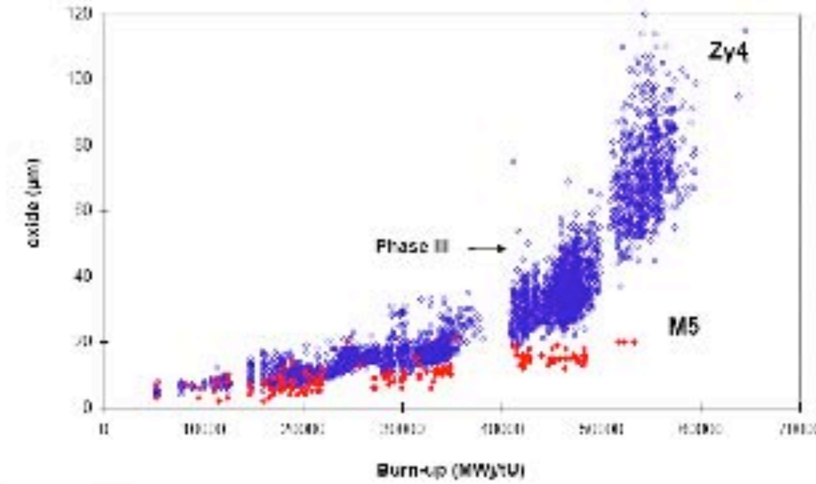
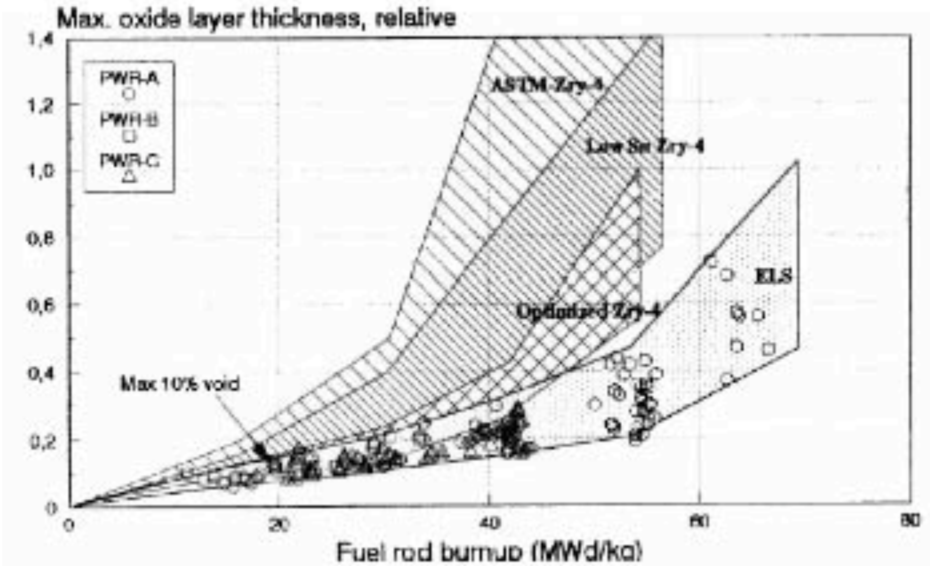
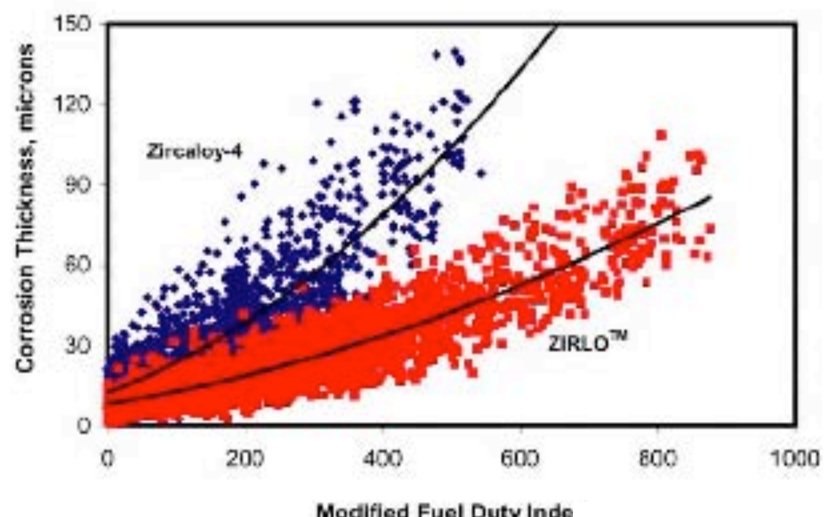
There are distinct variations in corrosion between zirconium alloys

- Uniform corrosion resistance is strongly dependent upon the chemical composition and the microstructure of the Zr alloy
- M5 (Binary alloy with fully recrystallized microstructure) appears the most corrosion resistant while CWSR Zircaloy is the less resistant







Source: B. Cheng

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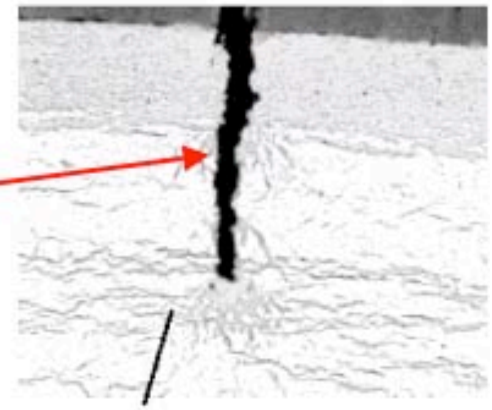
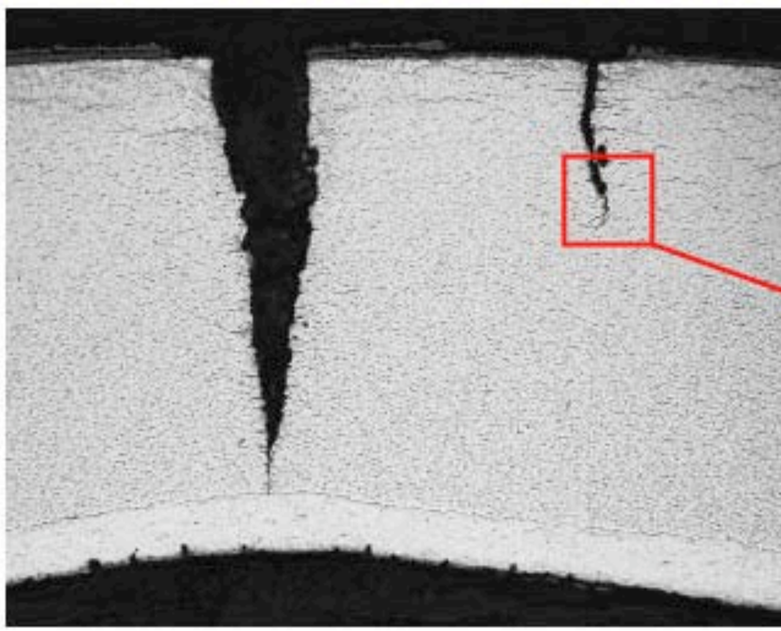
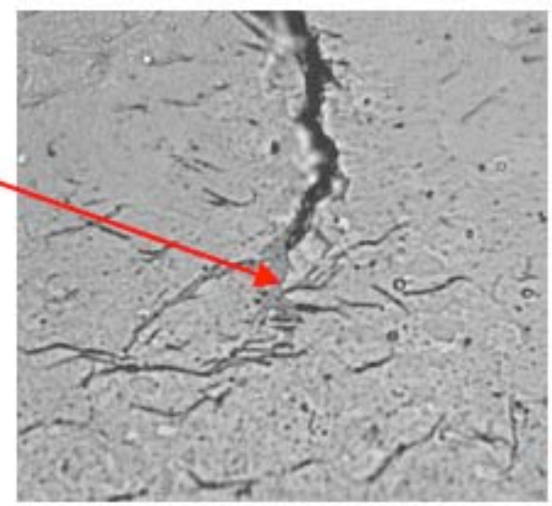
Hydrogen pickup leads to hydriding and hydride cracking

- **Fracture proceeds by Delayed Hydride Cracking (DHC) mechanism**
  - **Phenomenon might be activated under decreasing temperature, for instance during Dry Storage**
  - **The pre-existence of a crack is required (For instance, initiation in hydride rim under reactor operation)**
  - **Propagation of the crack is assisted by hydrogen diffusion and hydride precipitation at the crack tip**



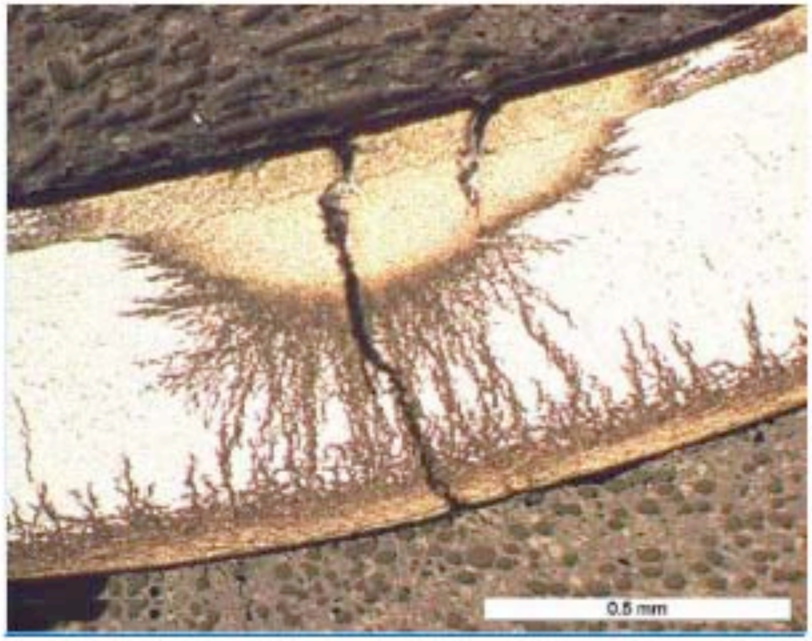


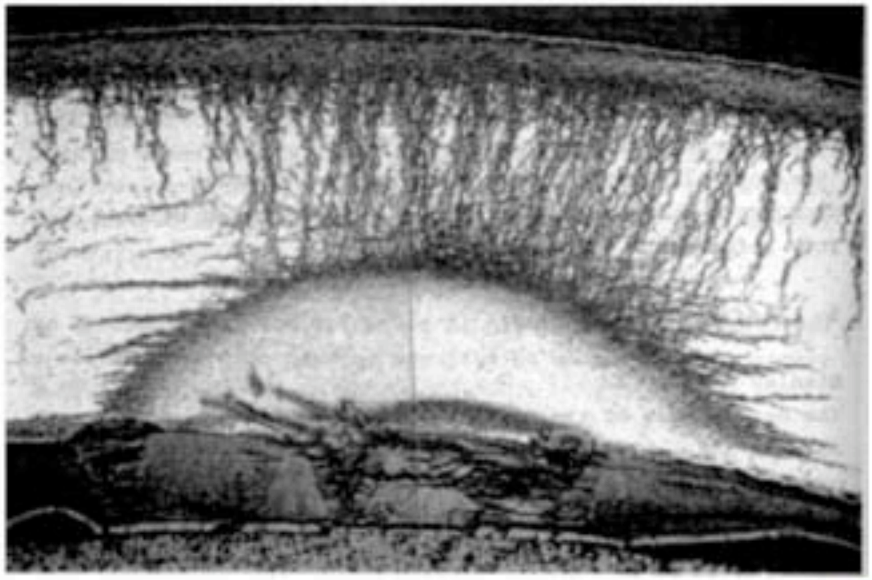


Source: B. Cheng

Secondary-degradation can lead to "sun-burst" hydrides

- Secondary degradation results from water ingress in the fuel rod after primary failure (PCI, fretting, CILC)
- Water causes oxidation of the inner surface of the cladding as well as of the fuel pellet
- Significant amount of hydrogen is produced which is picked up by the cladding at some distance away from the primary defect
- Hydride Sun Burst can be formed leading to the perforation of the cladding





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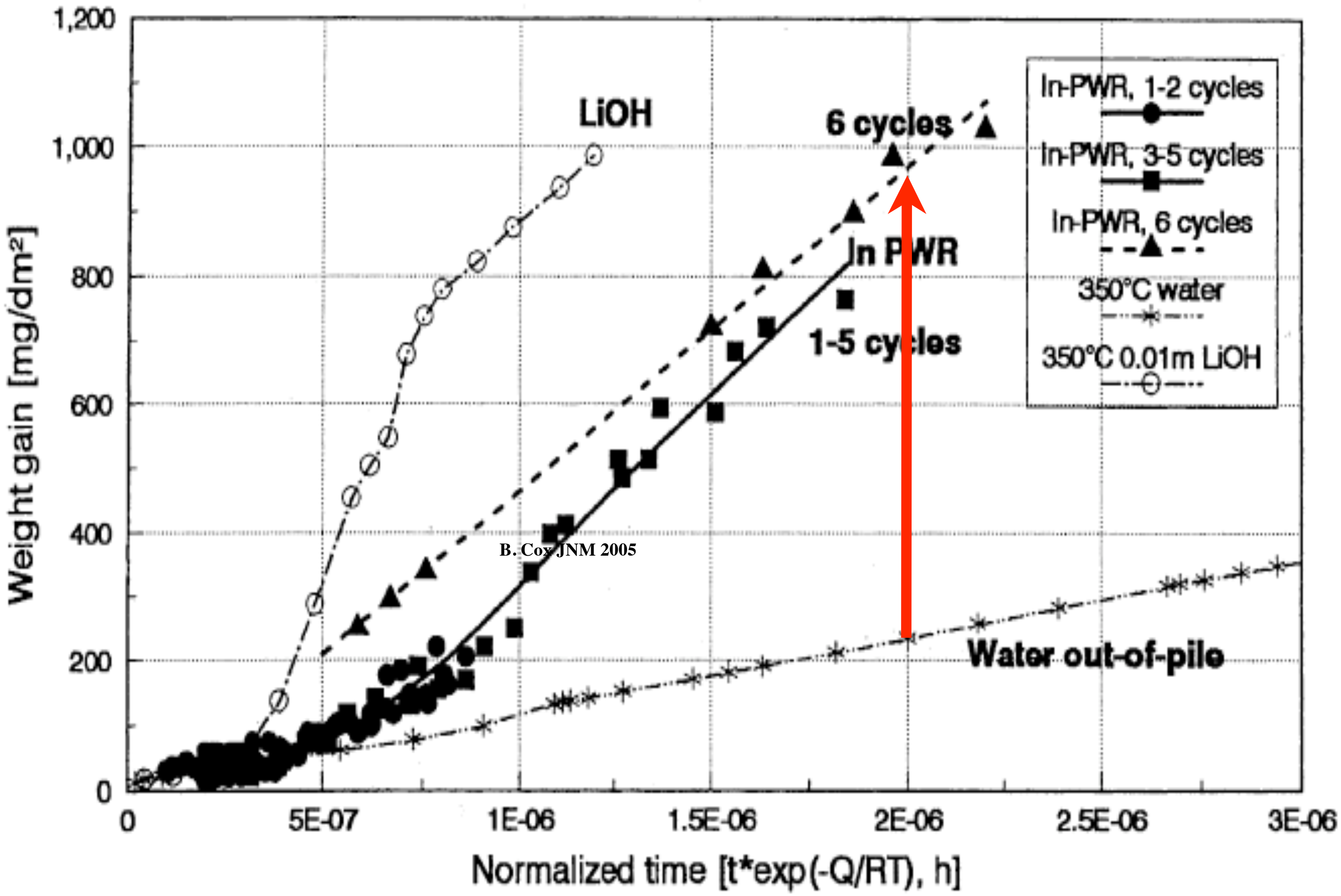
Irradiation-enhanced oxidation in zirconium alloys



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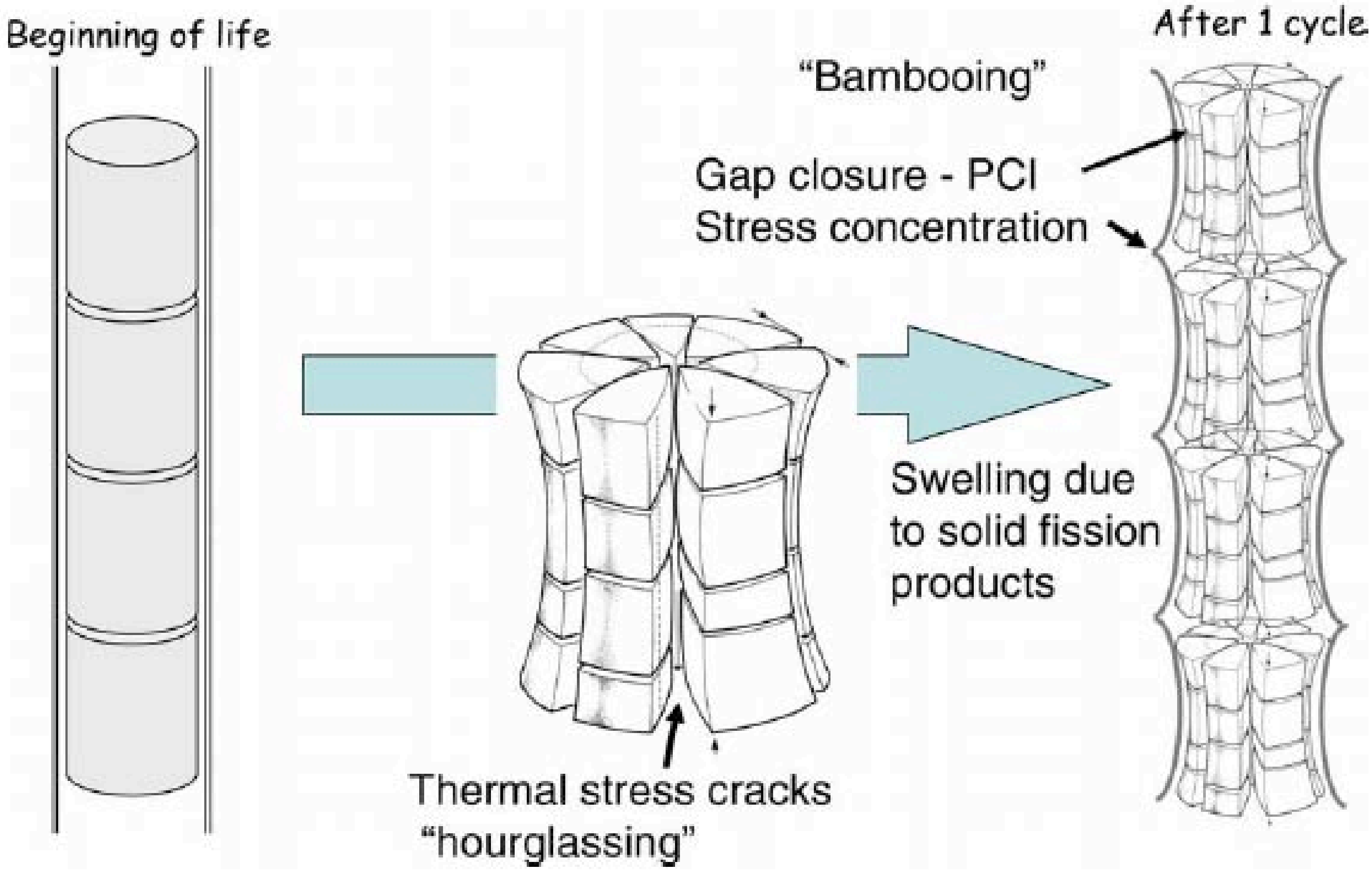
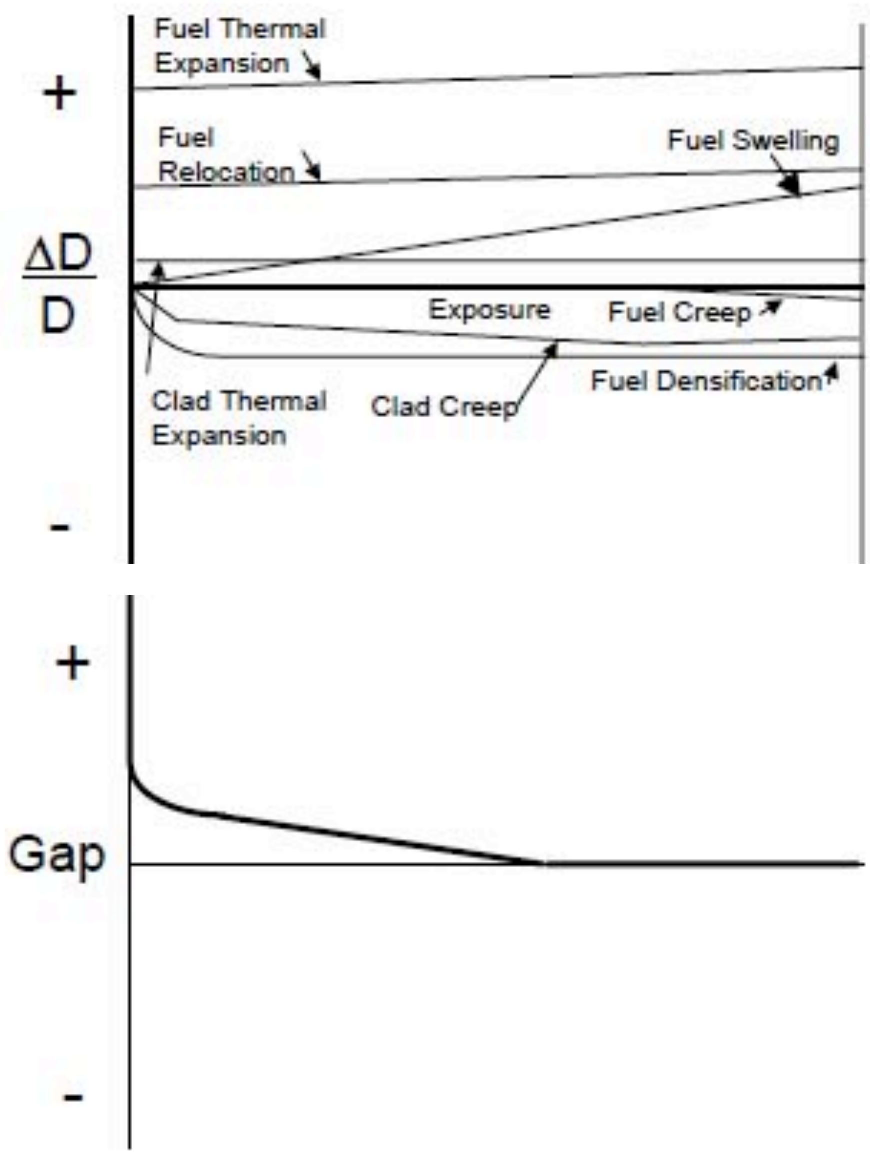
PCI in Zircaloy Fuel Cladding

Effects of thermal expansion and fuel swelling



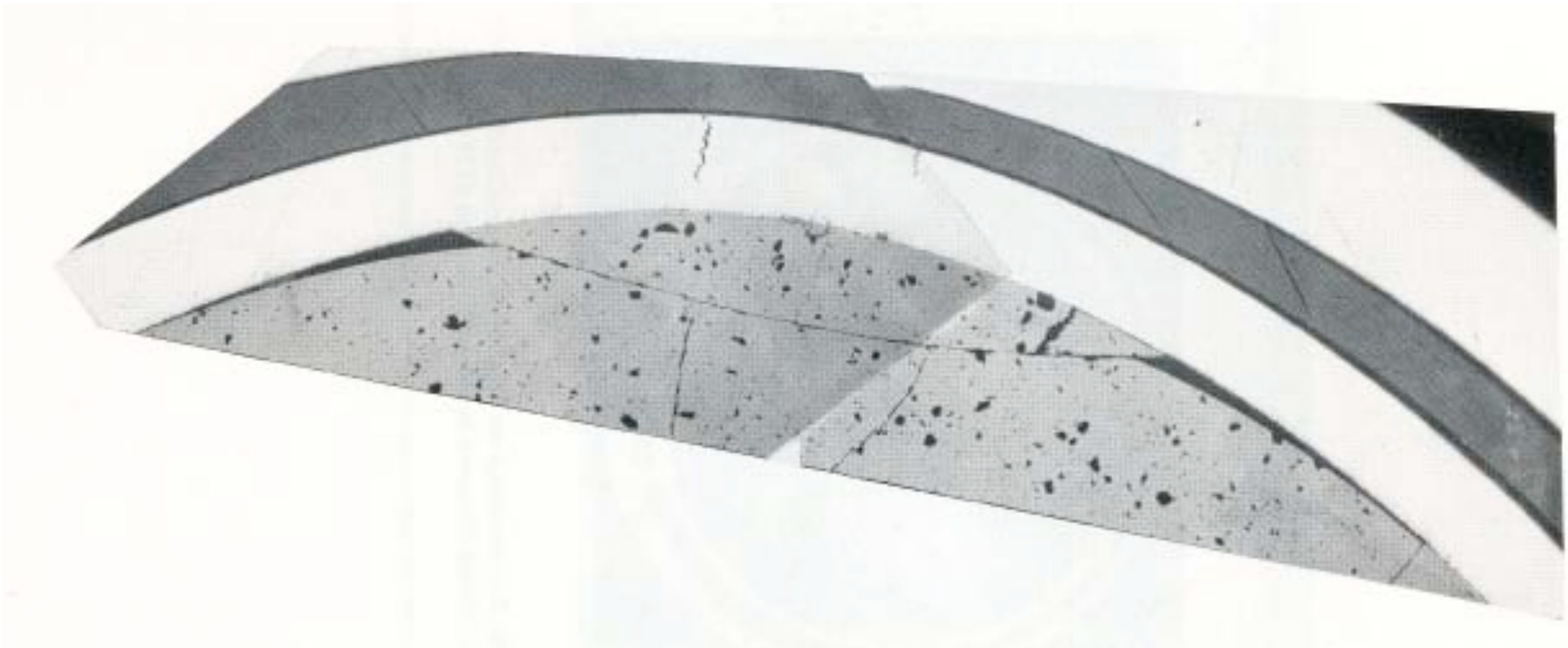
Source: B. Cheng

Additional sources of stress in PCI



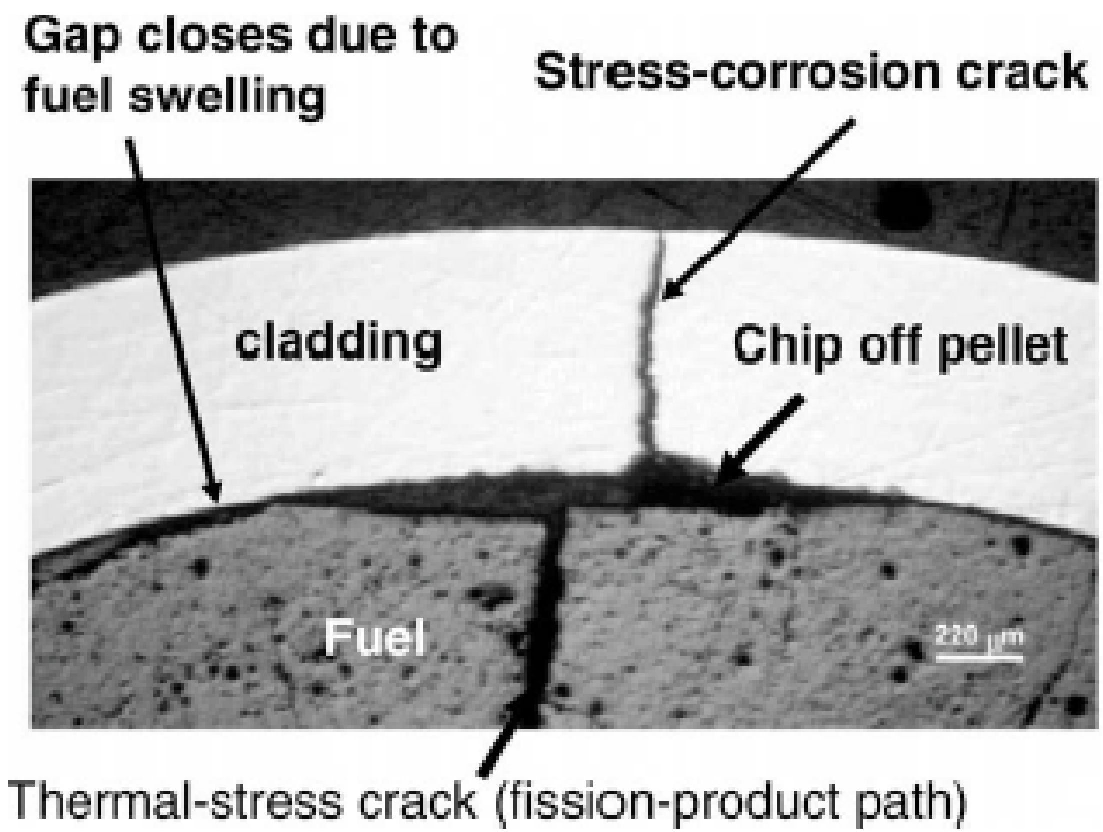
Source: D. Crawford

SCC on OD of stainless steel cladding caused by pellet-clad interaction (PCI)



EPRI NP-2119

SCC on the ID of Zircaloy cladding caused by pellet-clad Interaction (PCI)



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Managing Corrosion in Reactors

- *Materials selection*
  - select materials that are appropriate for the environment
  - control microstructure through processing/heat treatment

- *Environment control*
  - maintain a low corrosion potential
  - minimize impurities
  - keep conductivity low

- *Engineering design*
  - minimize residual stresses
  - avoid dissimilar metal welds
  - avoid crevices
  - surface finish

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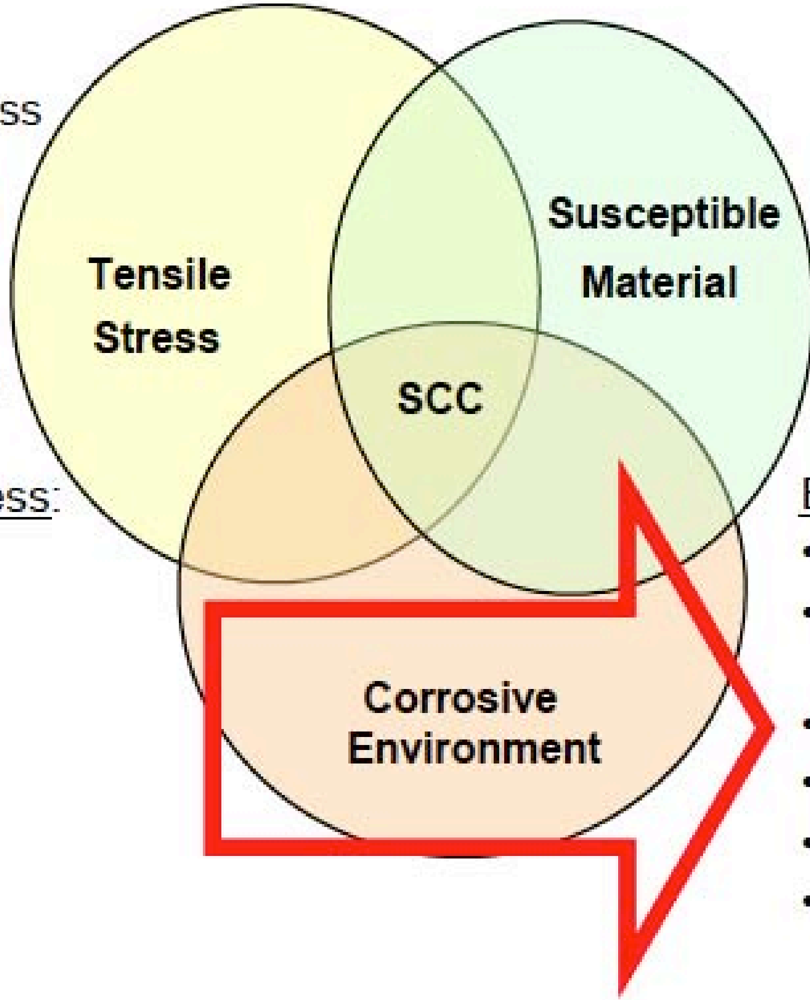
Managing Corrosion in Reactors

Increasing tensile stress decreases time for crack initiation and increases the propagation rate of pre-existing cracks



Susceptible BWR Materials:

- Alloy 600
- Alloy 182
- Alloy X750
- SS 304
- SS 304L and 316L
- SS 347, 321, 348

Sources of tensile stress:

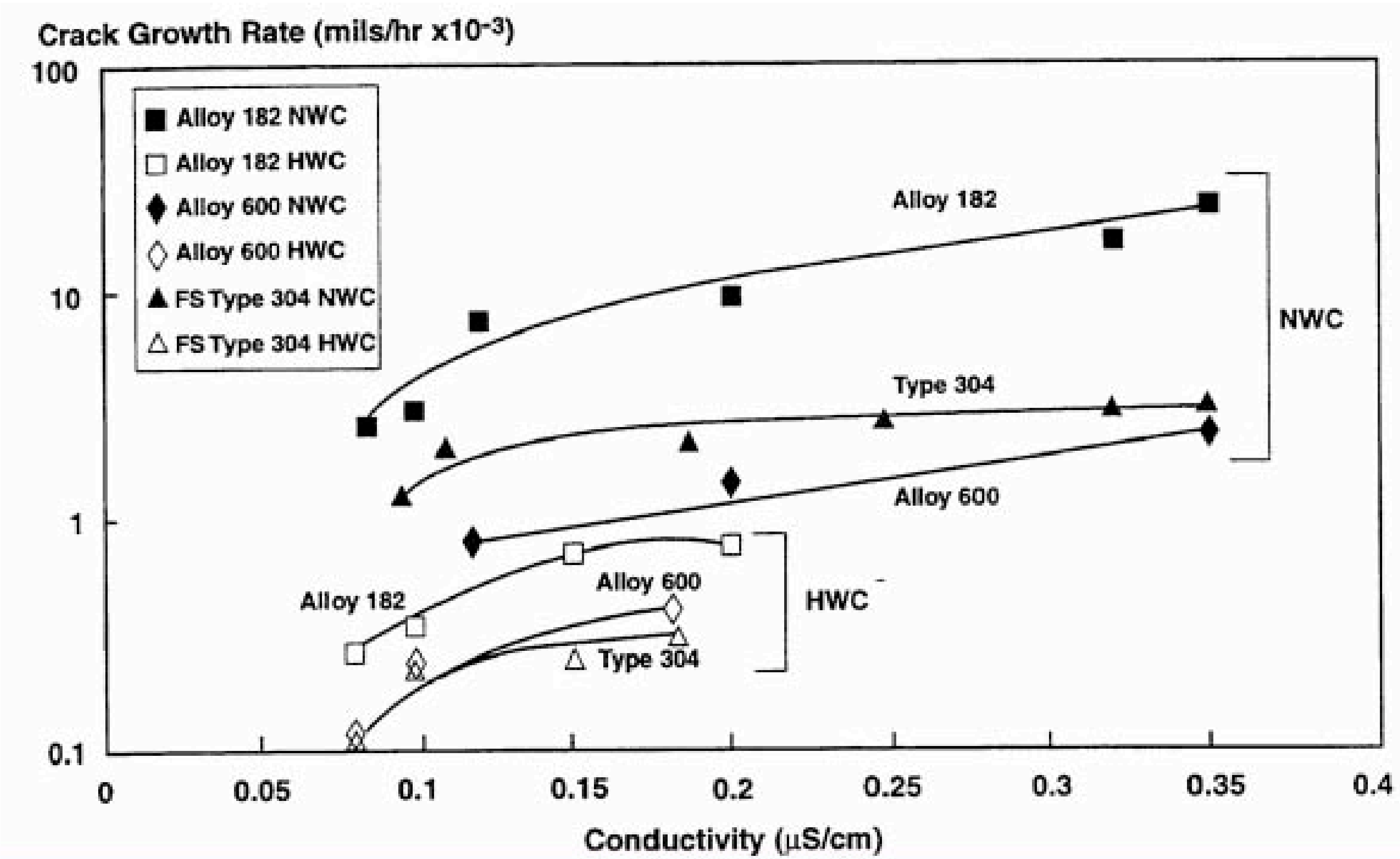
- Applied
- Residual
- Thermal
- Welding
- "Oxide Wedging"

Environmental Considerations:

- Water quality (impurities)
- Radiolysis/oxidant concentrations
- Temperature
- Surface treatments
- Flow rate
- Irradiation

Source: K. Fruzzetti

Managing Corrosion in Reactors



Even the PUREST water will NOT provide IGSCC immunity in the BWR - good water quality delays initiation, but IGSCC still occurs.

Source: K. Fruzzetti

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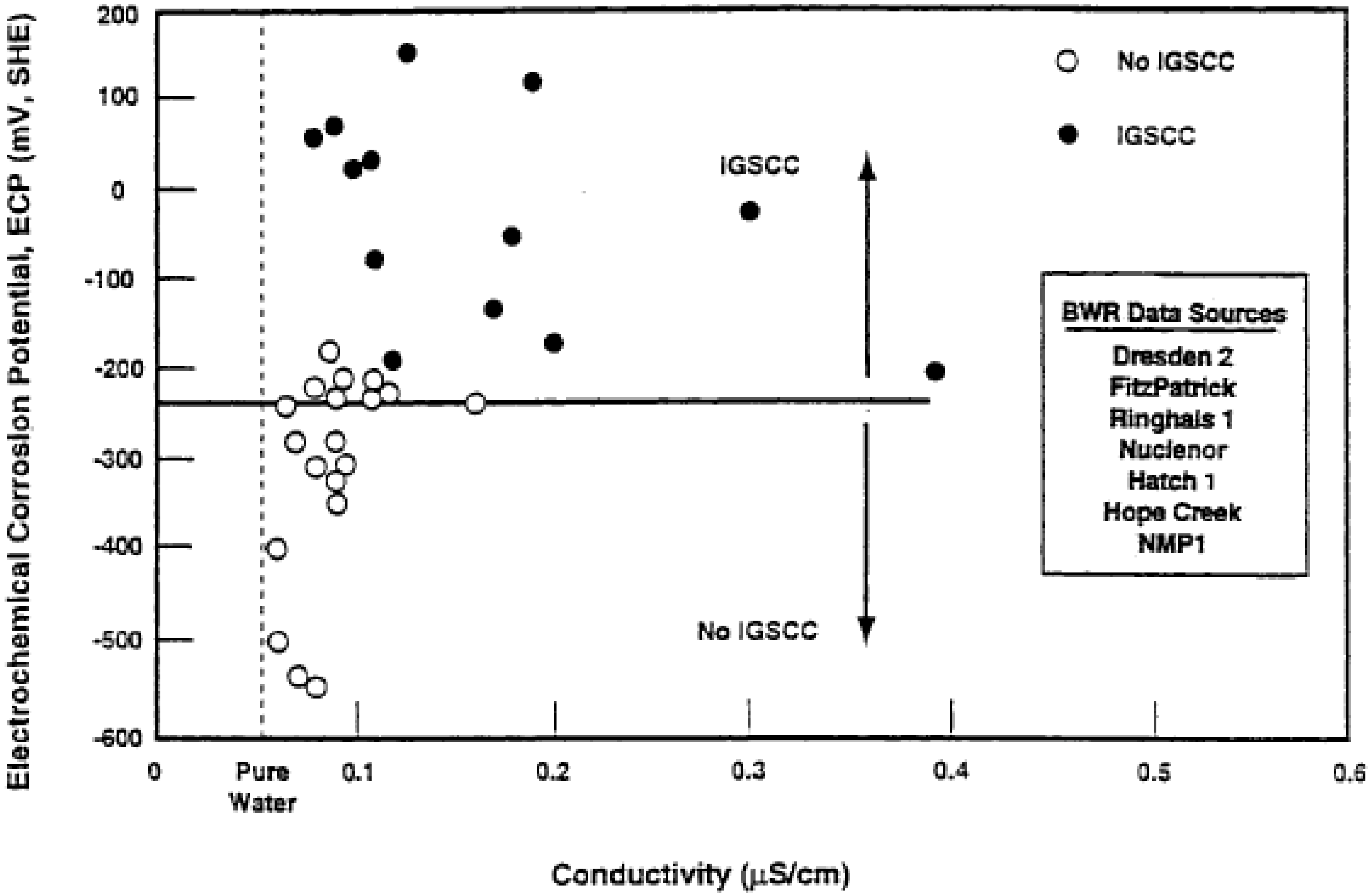
Managing Corrosion in Reactors

- *PWRs*
  - pH control to control corrosion
  - hydrogen addition to suppress corrosion potential on the primary side
  - minimize impurities on secondary side

- *BWRs*
  - hydrogen water chemistry to suppress corrosion potential
  - noble metal addition
  - TiO_2 technology

Examples of BWR water chemistry strategy evolution

BWR IGSCC Mitigation using HWC



Source: K. Fruzzetti

Beyond HWC alone

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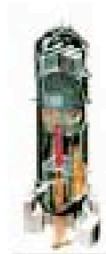
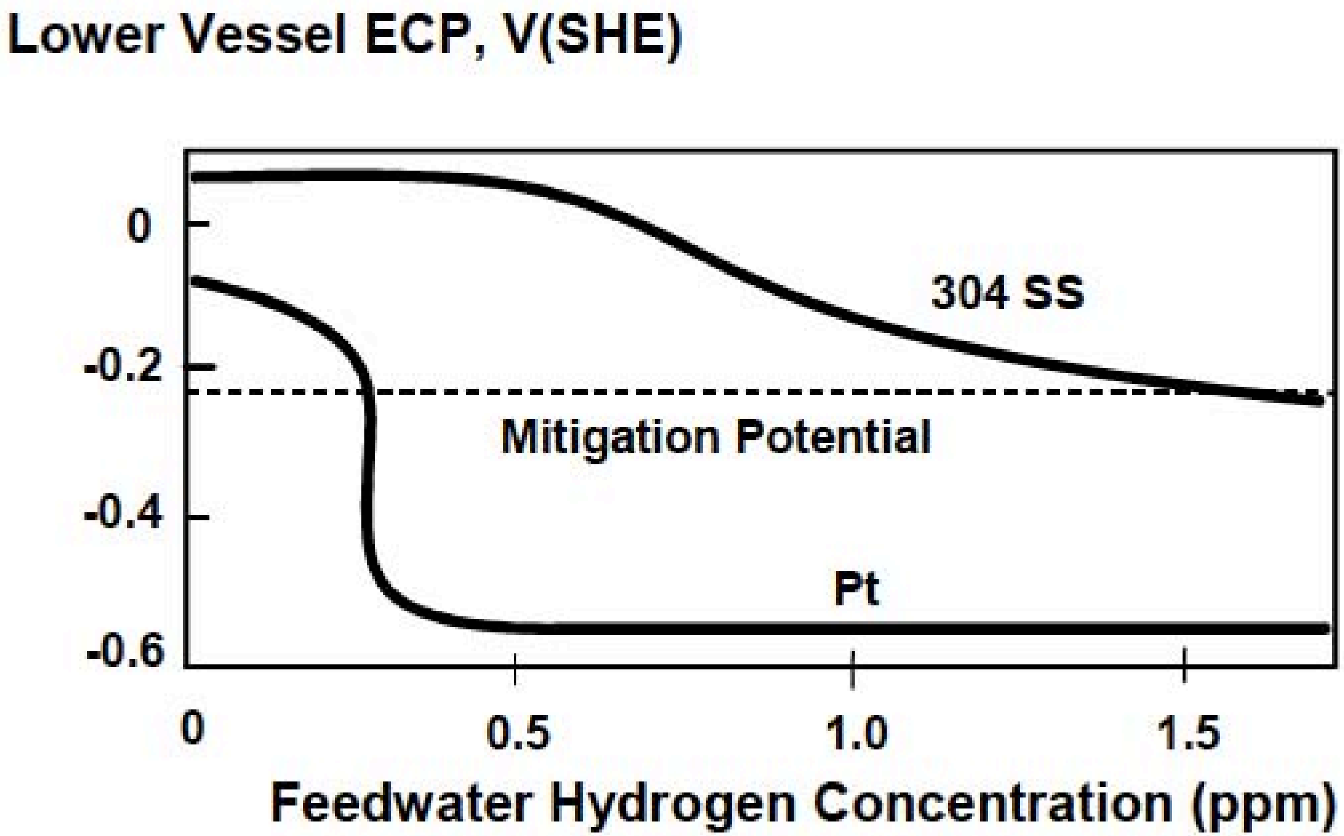


= NMCA



How to make stainless steel react as if it was Pt?

Answer: Incorporate Pt onto the surfaces.

Source: K. Fruzzetti

HWC and noble metal additions

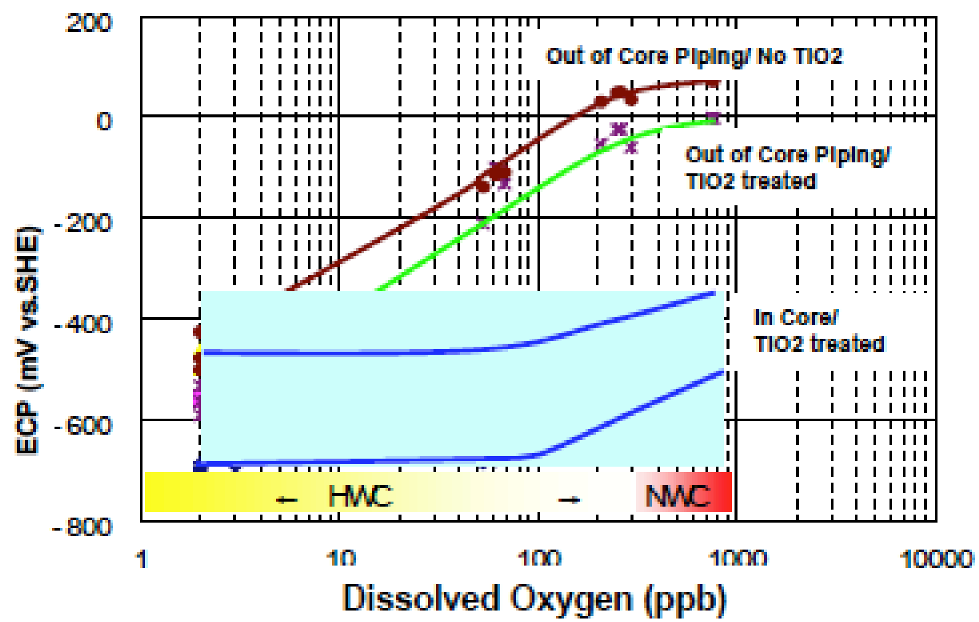
- HWC effective for IGSCC Mitigation (all U.S. BWRs applying)
- Adding noble metals results in catalytic surfaces and reduces amount of hydrogen needed by factor of ~4 or more
- Noble metals can be added 3 ways:
  - During plant shutdown (hold process) (NMCA)
  - During normal full power operation (OLNC)
  - To piping surfaces (after a decontamination) (LTNC)
- Majority of U.S. BWRs now apply noble metal (29 of 35 to date)

….but hydrogen is not always being injected at BWRs

Source: K. Fruzzetti

TiO_2 technology for IGSCC Mitigation

- Toshiba/TEPCO technology
- Cathodic reaction by photo excitation reaction
- Expected to mitigate SCC of components exposed to UV
- ECP decrease to <-230mV
- No hydrogen addition is required for reactor internals mitigation
- Expected advantages:
  - No main steam radiation increase
  - Effective for almost all reactor internals
  - No crack flanking for reactor internals
  - Compatible with HWC and/or Noble metals
- Application at 2-F-1 plant in June 2010, evaluation of plant response is ongoing



ECP of TiO2 treated stainless steel in the Halden Reactor Loop

Source: K. Fruzzetti

MichiganEngineering

ATR National Scientific User Facility

CMSNF Center for Materials Science of Nuclear Fuel

Summary

• Aqueous corrosion is an electrochemical process in which the metal ***and*** the solution play equally important roles

• Corrosion takes many forms; general, galvanic, localized, SCC, CF, hydrogen, FAC, Erosion, MIC…..

• Material selection must include the response the environment

• Environments are often dictated by one component, but can affect others

• Corrosion in LWRs covers the full space of corrosion modes, and differs between plant types, conditions, components, etc.

Summary

• Management of corrosion includes accounting for:

- material
- environment
- external factors; stress, irradiation, etc

• Management of corrosion is not an insurmountable task, but it needs to be done as a preventative measure - when the systems are planned - not after they're built!

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